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Comparison of doped combination zirconium-tungsten, zirconium-molybdenum and molybdenum-tungsten on single-wall vanadium oxide nanotube in hydrogen gas adsorption

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Abstract

In this study, doped vanadium oxide nanotubes were evaluated using different software to study the absorption of hydrogen gas. Vanadium oxide nanotubes are one of the options for absorption and storage hydrogen gas. In this research study for the first time, the Monte Carlo simulation was used to investigate the hydrogen gas absorption behavior in molybdenum-tungsten, molybdenum-zirconium and zirconium-tungsten doped vanadium oxide nanotub. At 300 K and at different pressures, the amount of hydrogen gas absorption inside and outside the doped nanotubes has been investigated. The results show the maximum adsorption capacity in 50MPa. Also, by comparing the obtained data and absorption isotherms, was determined absorption of hydrogen gas in vanadium oxide nanotube doped with zirconium molybdenum was better than the other two nanotubes.

Keywords: Simulation Monte Carlo (MC), Vanadium oxide nanotube (VONT), absorb,

1. Introduction

Carbon nanotubes, is the first of group nano-tubes, which was described in 1991 by Iijima. Subsequent significant efforts were made to synthesize nanotubes. The presence of carbon atoms in the structure of nanotubes created new physical and chemical properties that brought new applications and products. When the first paper on tungsten disulfide nanotubes (WS_2) was published in 1992, it was considered a very important approach in the field of nanotechnology. Although the geometry of inorganic nanotubes is similar to carbon nanotubes, there are two basic problems with using these nanotubes: one is the size control (dimensions) and the other is their purification. On the other hand, different applications of inorganic nanotubes in the electronics industry, catalytic reactions, energy storage, gas absorption, switches, etc. have attracted more attention from scientists. For example, the inorganic nanotubes (1992) WS_2 (1993) MoS_2, (1995) BN, (1998) SiO_2, (1998) TiO_2, (1998) VO, (1998) $NiCl_2$, (2000) NbS_2, ... were Synthesized [1]. The first samples from inorganic nanotubes are synthesized molybdenum and tungsten sulfides prepared by Tina and et al. These layered sulfides form structures of fullerene and then nanotubes. Several methods have been reported for the preparation of molybdenum and tungsten sulfide and selenide nanotubes in recent years. The synthesis of boron nitride nanotubes has attracted much attention due to the similarity of the structure of boron nitride to graphite. Over the past few years, nano-tubes have been produced from several inorganic materials such as binary oxides, nitrides, halides, and metal and non-metallic elements. In addition the nano-tubes with binary compounds, nano-tubes with complex compounds such as proioscites, titanates and spinels have been reported. Several methods have been used to synthesize inorganic nanotubes. In the case of tungsten and molybdenum sulfides, the analysis of the precursor compounds such as threesulfides and ammonium thiametalates or selenomethatels has been successful. An important method of synthesizing oxide nanotubes is the thermal and saloothermal (water-thermal and fluid-thermal) water treatment methods used in the presence of surfactants or other additives. The creation of sparks or arcs and laser lawns have been used to synthesize boron nitride nanotubes and other materials [2].

One of the types of inorganic nanotubes is vanadium oxide nanotubes. Vanadium oxide nanotubes were synthesized by Spahr in 1998. Vanadium oxide nanotubes consist of roller layers (V-O) and have a scroll-like structure. The end of this nano scrolls is open. The characteristic sizes and interlayer distances in vanadium oxide nanotubes are controlled by properly choosing the initial vanadium precursor and the structural template. The specific structure of vanadium oxide nanotubes has led to many applications in the microelectronics industry [3] and micro-sensors [4], catalysts [5] and sub-sources of electrical currents

[6][7]. Due to the openness of the end of these nanotubes, various cations can be incorporated into the interior of the nanotubes, the doping of metals into these nanotubes improves its properties and results in more applications in terms of performance. For example, Mai group (2003), Jiao group (2006), Li group (2007) and Rouhani (2011) were doped elements such as molybdenum, tungsten, copper and rhenium on vanadium oxide nanotubes [8-11]. Considering the improvement in the performance of vanadium oxide nanotubes with doping, one of the most important applications in this area, which is the absorption of hydrogen gas, is taken into account.

Hydrogen gas fuels can be used as an energy source for electronic devices [12]. Hydrogen gas is of great importance because it is reversible and clean, as well as its high internal energy relative to other fuels [13]. One of the problems for use of hydrogen energy is its storage. Therefore, the absorption and storage of hydrogen by different methods were considered as fuel. Liquefaction methods, compression methods, and using solids have been used for hydrogen storage [14], [15]. In the liquefaction process, is required a refrigeration system that is economically cost to determine the low temperature. In a state of hydrogen compression, the security problem is very serious. So researchers considered solid materials for an appropriate storage factor. Different materials, such as metal hydrides [16], carbon nanotubes and nano-horns [17], inorganic nanotubes, such as oxide-metal nanotubes [18], were considered. Metal oxide nanotubes are used in catalytic processes, electrochemical equipment, and Nano sensors [19]. Intermediate metal oxides are of interest due to their physical and chemical properties.

Vanadium oxide nanotubes, are a group of oxide nanotubes, that have been widely studied. The structure of these nanotubes resembles carbon nanotubes [20]. Vanadium oxide nanotubes are synthesized at a low temperature and with a chemical process [21]. Due to the closure of carbon nanotubes ends, there have a low absorption of hydrogen gas, so absorption is only done on the outer surface of the nanotubes. The size of the nanotubes and the walls between in the vanadium oxide nanotubes is controlled by selecting the type of material and the structure of the amine used. The end of these nanotubes is open [22]. The cave mode, like these nanotubes, provides conditions for the entry of molecules into the nanotubes.

Nanostructures with high porosity and internal porosity have high absorbency and storage capacity [23,24]. Hydrogen gas absorption on vanadium oxide nanotubes has been done with different volumetric and electrochemical methods, with increasing pressure from zero to10 bar, hydrogen uptake has increased on VONTs [25].

In this study, using the Monte Carlo simulation, were investigated the hydrogen gas absorption capacity in vanadium Oxide nanotube doped combined with zirconium, molybdenum and tungsten elements at 300 K and different pressures (0.5-50) MPa.

2. Computational details

In this study, calculations were performed in two parts of quantum mechanics and molecular mechanics. Quantum mechanical calculations were used to optimize vanadium oxide nanotube as shown in Figure 1. The atomic models of the VONT are cut from a orthorhombic V_2O_5 crystalline which consist of layers VO_5 square pyramids that share edges and corners. Vanadium oxide nanotube with a length of 12.33 Å and diameter 12.95 Å was performed using the nanotube modeler. Combines doped of zirconium, molybdenum and tungsten elements (10%at) done on vanadium oxide nanotube. In the next step, using the material studio software and the DFT computational method with the generalized-gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) of the nanotube were optimized [26][27]. After optimizing the vanadium oxide nanotubes (Figures 2and3), using the molecular mechanic and the Monte Carlo simulation software, the hydrogen gas adsorption capacity was calculated on doped vanadium oxide nanotubes. In fact, the effect of pressure changes was investigated on the absorption of hydrogen molecules in the nanotubes. To determine the thermodynamic quantity, the absorption capacity of the gas-to-nanotube interaction in the Monte Carlo simulation (MC) was performed using the Metropolis Algorithm [28]. The process of implementing this simulation using a cubic box (with the edge of 50Å), which contains the single-wall vanadium oxide nanotube in its center (Fig 6). Hydrogen gas molecules are considered as spherical particles, which in the thermodynamic conditions in this study have an ideal behavior.

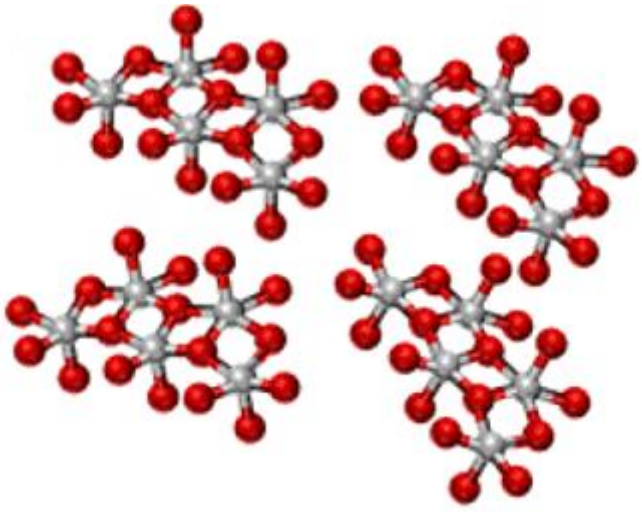

Fig 1:Vanadium oxide (V_2O_5)

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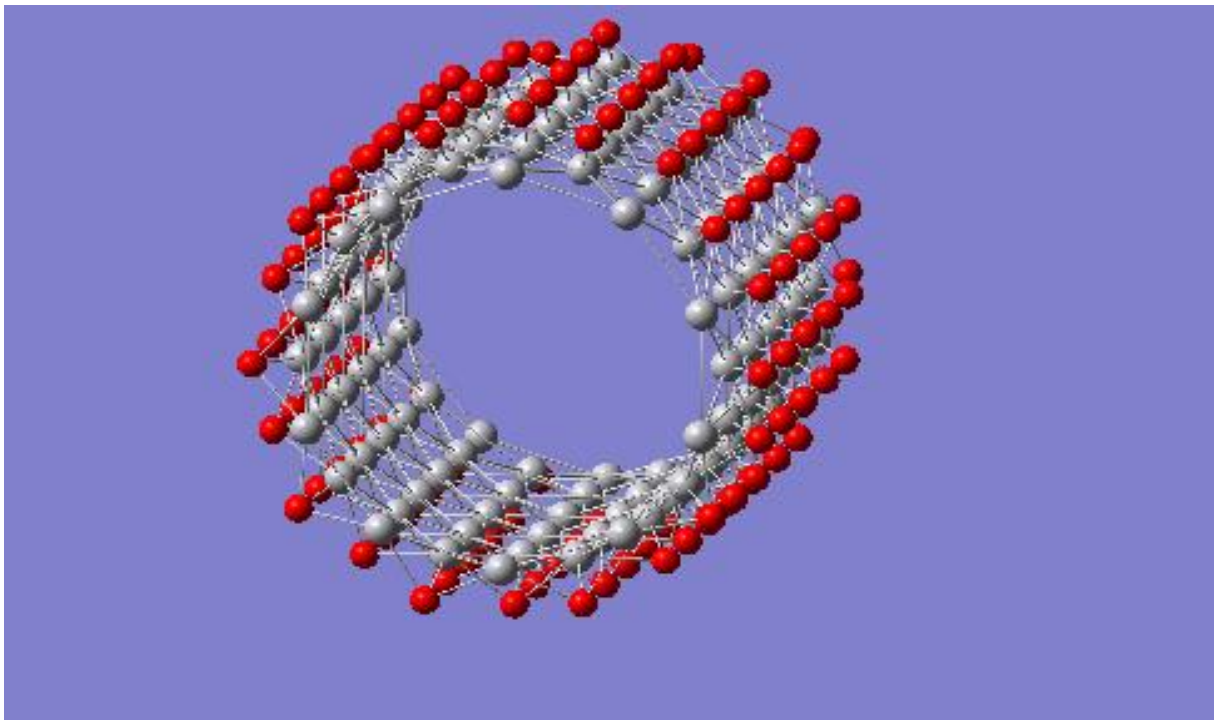

Fig2: Cross section of optimized vanadium oxide nanotube

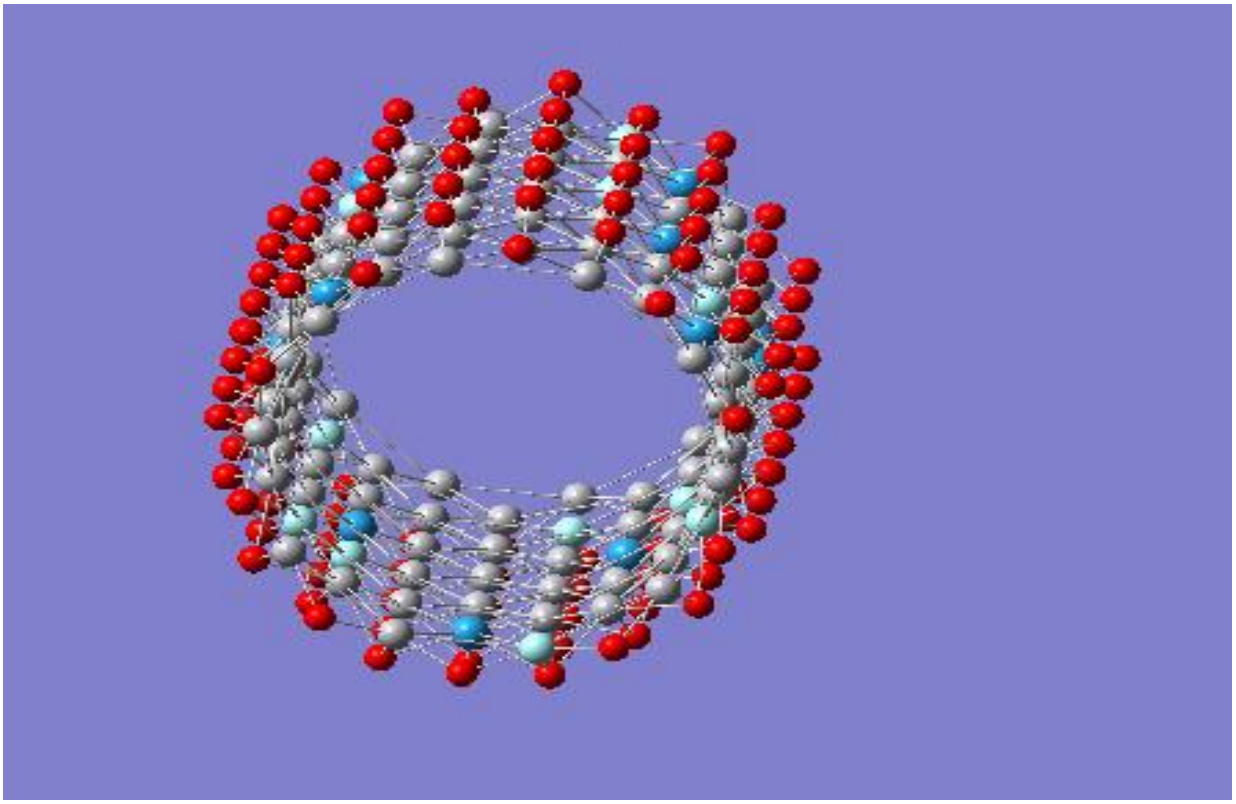

Fig3: Cross section of optimized doped vanadium oxide nanotube

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3. Results and discussion

The adsorption isotherms were computed using a grandcanonical ensemble, generated via MC steps. Temperature, pressure and nanotube type are considered as parameters to influence the adsorption process. Therefore, effect of pressure on the adsorption capacity of doped VONTs were evaluated to predict the best structure for hydrogen storage. We applied the Monte Carlo simulations in order to find out the gravimetric adsorption capacity of hydrogen in the NTs under different conditions.

The gravimetric adsorption capacity for pure gases is demonstrated according to the following equation:

$$\rho_w = \frac{N_H\, m_H}{N_H\, m_H + N_{NT}\, m_{NT}}$$

Where m_H and m_{NT} denote the molar mass of hydrogen molecules and atoms in NTs,respectively, and N_H and N_{NT} represent the number of hydrogen molecules and each atom type in NT. Gravimetric adsorptions of H2 inside and outside of all VONTs(Mo-Zr, W-Zr and W-Mo doped VONTs) were computed in different pressure at 300K (Table 1).

Hydrogen gas adsorption isotherms are compared on doped vanadium oxide nanotubes with zirconium-molybdenum, zirconium-tungsten and molybdenum-tungsten at different pressures of 0.5 to 70 MPa in Figures (4 and 5). As shown in the figures, with increasing pressure, the number of hydrogen gas molecules increases, followed by an increase in the absorbed hydrogen density. Therefore, with increasing pressure, the percentage of adsorption increases. The maximum absorption value is at 50 MPa (Fig 6), which is fixed after this absorption pressure. In other words, in this pressure, the nanotube is saturated. Reducing adsorption at pressures higher than 50MPa is due to the low space inside the nanotube, which results in reduced entropy (Fig5). Among the graphs of the combined temperature of these elements, the process of absorbing hydrogen gas is the same for all the desired nanotubes. Though nanotube doped with tungsten-zirconium has less absorption than two other nanotubes. The vanadium oxide nanotube doped with molybdenum-tungsten up to a pressure of 40 MPa has the highest percentage of absorbance compared to the other two nanotubes, but slightly decreases from 40 above relative to the molybdenum-tungsten doped vanadium oxide nanotube. The electron densities of intermediate metals together lead to different interactions in different pressures.

The molybdenum-zirconium doped vanadium oxide nanotube has a higher uptake and more regular trend than the other two nanotubes.

Table 1: Gravimetric adsorption capacities inside and outside the VONT-(M_1+M_2) at 300 K

P(MPa)	VONT-(MO+Zr)		VONT-(MO+W)		VONT-(W+Zr)	
	Inside	Outside	Inside	Outside	Inside	Outside
0.5	0.001387	0.00061	0.000824	0.000464	0.00082	0.000419
1	0.002604	0.001267	0.002182	0.001104	0.001479	0.000868
2	0.004647	0.002521	0.003777	0.00222	0.002746	0.001669
4	0.006879	0.005245	0.00546	0.00461	0.004035	0.003384
5	0.007201	0.006605	0.006443	0.00547	0.005099	0.004024
10	0.007016	0.008993	0.0086	0.09806	0.00669	0.007309
15	0.00836	0.01186	0.009281	0.01248	0.007666	0.009561
20	0.014328	0.014328	0.01076	0.01445	0.008319	0.01147
30	0.017491	0.017491	0.012441	0.01735	0.01039	0.016054
40	0.012516	0.019914	0.01067	0.01725	0.01039	0.016054
50	0.012761	0.022048	0.01124	0.019074	0.011719	0.017737
70	0.014467	0.025715	0.01303	0.0222	0.013297	0.020885

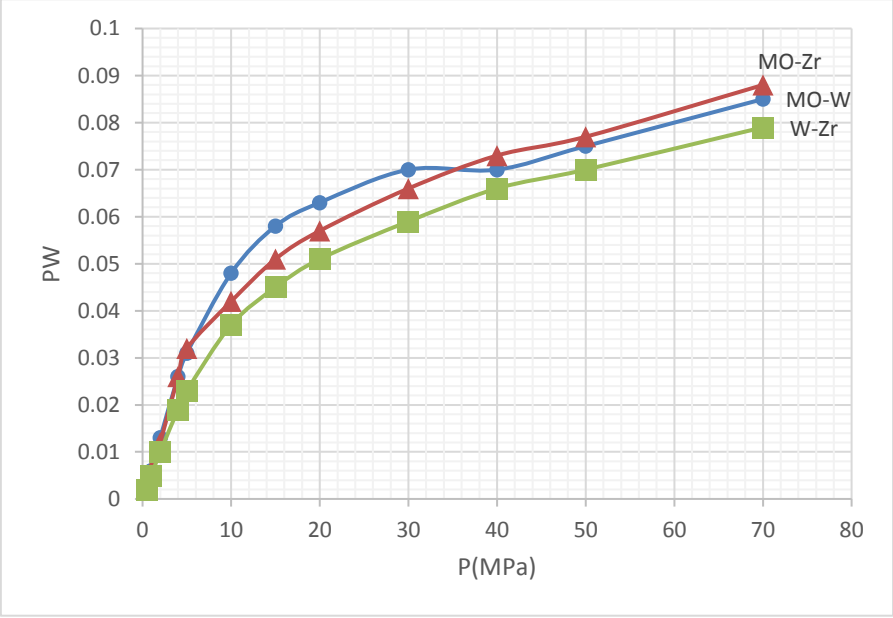

Fig4: comparison of adsorption isotherms of doped VONTs nanotubes at 300K-outside the nanotubes

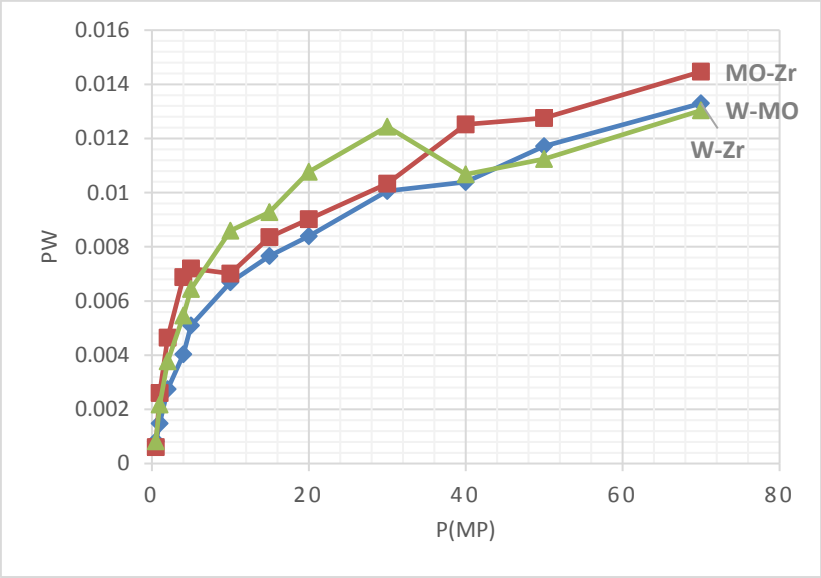

Fig5: comparison of adsorption isotherms of doped VONTs nanotubes at 300K-inside the nanotubes

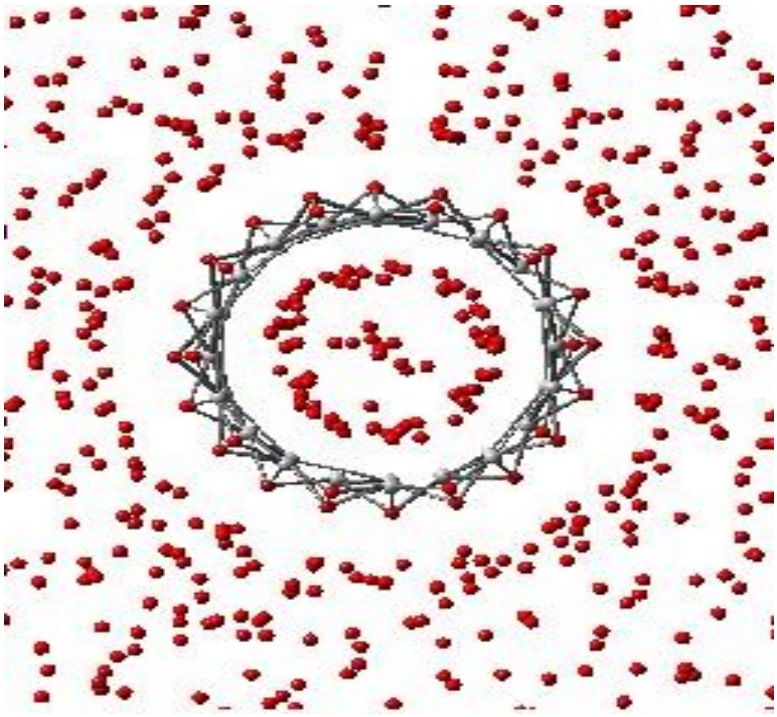

Fig6: Snapshot generated by the simulation of hydrogen adsorption at 300 K and 50 MPa

4. Conclusion

The adsorption of hydrogen in the VONT was investigated using molecular simulation approach.The temperature of 300 K and pressures of (0.5-70)MPa were considered. Hydrogen adsorption in VONT were comparable with other nanostructures.

Investigation of hydrogen gas absorption isotherms on molybdenum-zirconium, tungsten-zirconium and tungsten-molybdenum vanadium oxide nanotubes using Monte Carlo simulation showed that the highest amount of hydrogen adsorption on nanotubes was related to pressure50 MPa. Also, the calculations showed that the adsorption of hydrogen gas in the outside the nanotubes was higher than inside the nanotubes. Vanadium oxide nanotube doped with zirconium-molybdenum had higher absorbance.

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