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Study of Hydrogen Adsorption on FeTi Using Molecular Dynamics Simulations

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We have used molecular dynamics simulation to study the adsorption isotherms of molecular hydrogen on FeTi at several temperatures ranging from 60 to 100 K. Adsorption coverage, isosteric heat, and binding energy were calculated at different temperatures and pressures. The results indicated that FeTi can be used as an ideal hydrogen storage material. The surface coverage or total amount of hydrogen adsorbed on FeTi is between 0.28 to 0.35.

Keywords: FeTi, Molecular dynamics simulation, Adsorption, Isotherm

INTRODUCTION

Hydrogen as an ideal energy carrier has attracted a great deal of attention in recent years. Its application in vehicles and portable electronics is limited by the difficulty of achieving a capable storage method [1]. There are several hydrogen storage methods, including compressed gas, liquefaction, metal hydrides, and physisorption [2]. Despite numerous research efforts and many obvious developments, problems associated with the storage and transportation of hydrogen has remained unsolved. In the beginning, the metal alloys have been suggested as proper material for hydrogen storage [3]. Among different metal alloys, FeTi has been selected for practical employment, because it is lighter and cheaper than other rare earth metals [4]. However, the activation process limits its application in commercial use [5].

Subsequently, a number of experimental works and treatments have been performed to investigate the hydrogen adsorption on FeTi and improving its storage capacity. Morris and co-workers studied the production and initial evaluation of hydrogen storage alloys produced by physical vapor deposition and mechanical alloying. These techniques have been applied to FeTi alloys systems and results denoted that both methods greatly enhance the amount of hydrogen uptake and the ease of activation [6]. The FeTi alloy with a mixture of nano and amorphous structures was prepared by mechanical alloying of Fe and Ti metals using a planetary ball milling system. This alloy was applied to store the hydrogen produced by electrolysis using a wide mill and solar photovoltaic arrays [7]. Heller *et al*. investigated the kinetics of hydrogen uptake through Pd and Ni coating before and after air-exposure [8,9]. Although several experimental works have been performed, many fundamental aspects of hydrogen adsorption are still an active field of research and there is no sufficient theoretical interpretation for hydrogen adsorption on FeTi.

The theoretical calculation can be greatly helpful for

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understanding the adsorption procedure and for improving the storage capacity. Hydrogen storage on FeTi (110) surface with palladium monolayer was studies using the full potential Linearized Augmented Plane Wave method within the local density of approximation. With these calculations, Kulkova was able to predict the preferable surface orientation and composition [10]. Kinaci *et al*. have carried out a first principles search for a possible hydride with high hydrogen storage capacity in the FeTi intermetallic system [11]. Since FeTi is relatively low cost compared with other rare-earth metals, it seems that this alloy can be used as an inexpensive H_2 storage compound [12].

In this paper, the adsorption isotherms of molecular hydrogen were obtained using molecular dynamics simulation and adsorption coverage, isosteric heat, and binding energy for adsorption of hydrogen on FeTi were also calculated.

METHOD

Molecular dynamics simulations were performed using a modified Tinker 4.2 package [13] in the NPT ensemble. The Buckingham force field was used for describing the interaction between different atoms. The Dreiding potential [14] is defined as

$$E = D_0\left[\left(\frac{6}{\zeta-6}\right)e^{\zeta(1-\rho)} - \left(\frac{\zeta}{\zeta-6}\right)\rho^{-6}\right] \quad (1)$$

where D_0 is the potential well depth and ξ is a steepness factor, and ρ = r/x in which r is the interatomic distance and x is the interatomic distance at the minimum of the potential.

The potential parameters used in this work were taken from Ref. [15]. The experimental value of 0.368 a.u. was used for quadratic force constant of the hydrogen molecule [16].

The periodic boundary conditions were imposed in all three dimensions and van der Waals cut-off was chosen as 12 Å. FeTi has CsCl structure with a lattice constant of 2.96 Å [17]. The super cell of FeTi crystal contains 250 atoms, corresponding to 5 unit cells along x, y and z directions. The volume of simulation box is chosen as (50 × 50 × 50) $Å^3$. The initial configuration is randomly generated with the number of hydrogen molecules, and the simulation boxes include 25 to 1000 hydrogen molecules (Fig. 1).

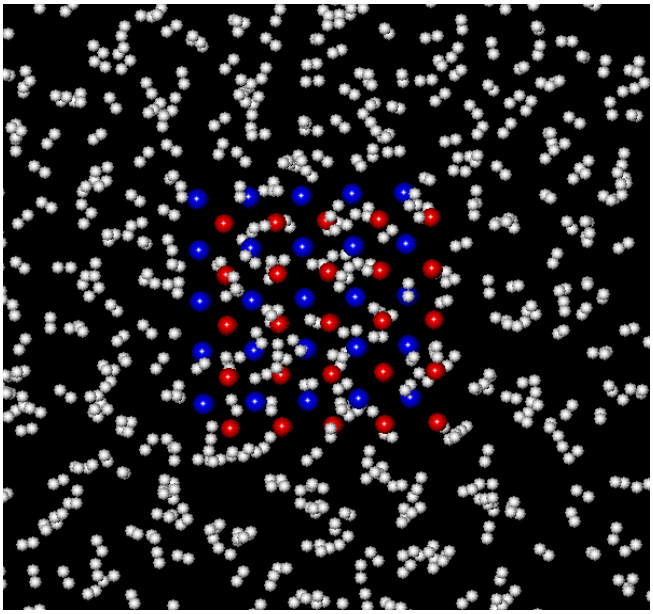

Fig. 1. Snapshot of initial configuration of simulation box.

First, the initial configurations were minimized and then the system was equilibrated for 100 ps followed by a 200 ps production run. The equations of motion were integrated by the Beeman method [18]. The integration time step is 1 fs. A Nose-Hoover extended system thermostat was used for the temperature control [19].

RESULTS AND DISCUSSION

Coverage of FeTi

A monolayer of H_2 on the external surfaces of FeTi is observed at low pressure. The first layer is filled completely by successive increase of H_2 molecules and after that, the second, third, and higher layers are formed. The distance between the surface of FeTi and the first layer of adsorbed hydrogen is about 6 Å, while the separation distance between the H_2 layers is 4.5 Å. First and second adsorbed layers of H_2 are shown in Fig. 2.

The adsorption isotherms of H_2 on FeTi for different number of molecular hydrogen at various temperatures and pressures were considered in this work. The adsorption coverage of H_2 on the FeTi has been expressed in terms of the atomic ratio of H_2 to FeTi (N_{H2}/N_{FeTi}). From our results, the

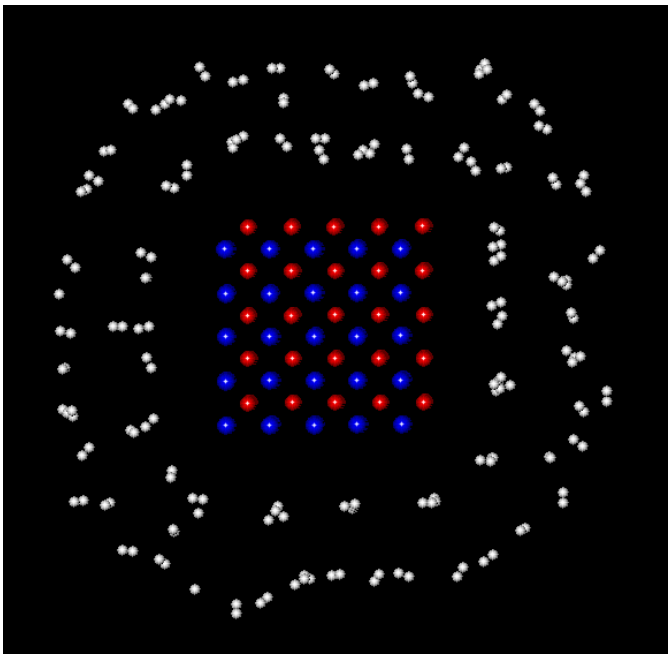

Fig. 2. Snapshot of first and second layers of H_2 adsorbed on FeTi.

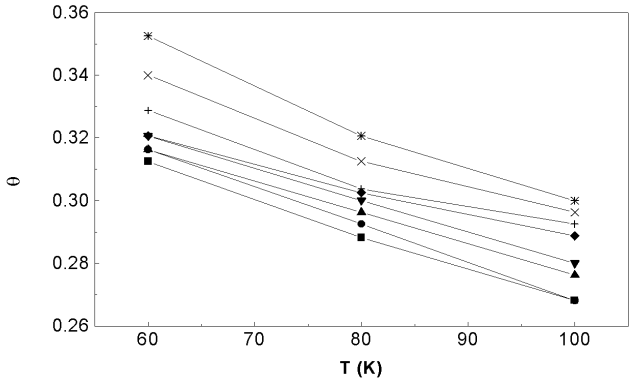

Fig. 3. Adsorption coverage as a function of temperature at different pressures (MPa): (✳) 1.0, (×) 0.5, (+) 0.1, (◆) 0.05, (▼) 0.01, (▲) 0.005, (●) 0.002, (■) 0.001.

adsorption coverage for the first adsorption layer decreases by increasing temperature (Fig. 3) and pressure (Fig. 4). The saturation coverage of the first exohedral monolayer adsorption is about 0.35, 0.3 and 0.28 H_2-FeTi at 60, 80 and 100 K, respectively.

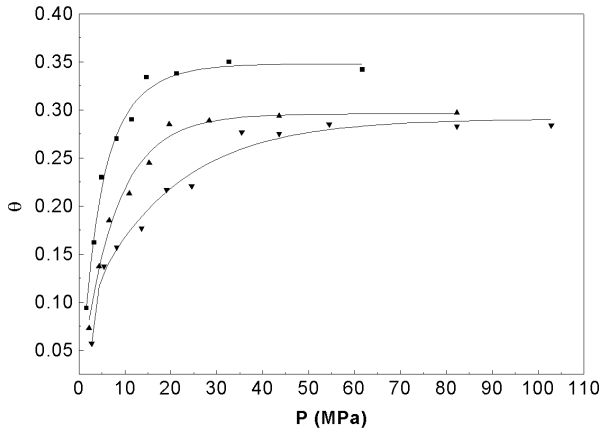

Fig. 4. Adsorption coverage as a function of pressure at various temperatures: (■) 60 K, (▲) 80 K, (▼) 100 K.

Heat of Adsorption

The isosteric heat of adsorption, q_{st} is the amount of heat released when an atom adsorbs on a substrate. It can be determined from the slope of the plot of ln p as *vs*. $1/T$ for a fixed amount of gas adsorbed on the substrate, as is given by equation (2) [20]:

$$q_{st} = -R\left(\frac{\partial \ln P}{\partial T^{-1}}\right)_{\theta} \tag{2}$$

where, q_{st} is the isosteric heat of adsorption of H_2, R is gas constant and θ denotes surface coverage or total amount adsorbed. The resulting ln p-1/T plots at different θ values are shown in Fig. 5.

The plot of isosteric heat of adsorption of H_2, q_{st}, as a function of coverage is shown in Fig. 6. As seen, q_{st} increases with increasing coverage due to attractive interaction with neighbor atoms. The isosteric heat reaches a maximum at about 1660 J mol^{-1} for θ = 0.23 H_2-FeTi. After the maximum value, the heat of adsorption decreased to 1500 J mol^{-1}, due to the repulsive forces among adsorbed hydrogen molecules.

It has been shown that the relation between isosteric heat of adsorption and binding energy, ε, is defined as [21]:

$$q_{st} = -\varepsilon + 2k_B T \tag{3}$$

where k_B is Boltzmann's constant and T is the average value of

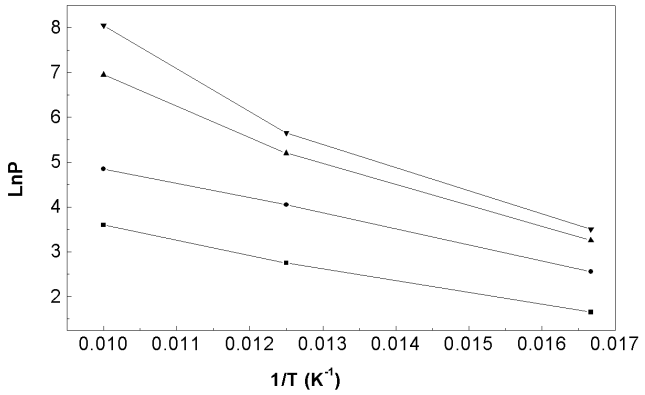

Fig. 5. ln *p* with the 1/T for different adsorption coverage of H_2 on FeTi, θ. The θ values are: (■) 0.084, (◆) 0.12, (▲) 0.15, (▼) 0.16.

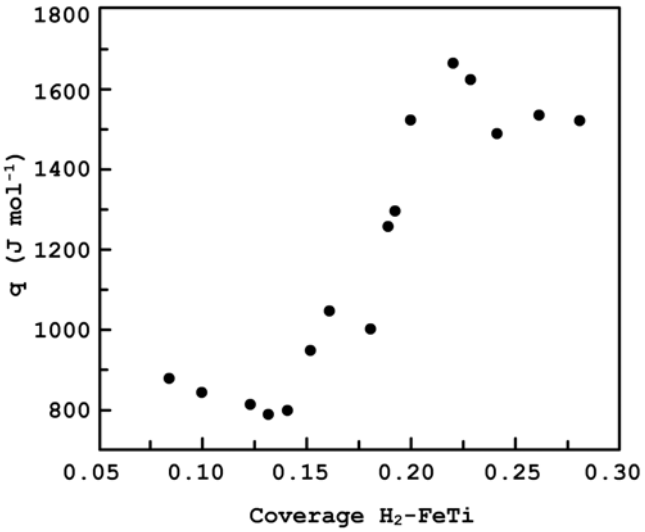

Fig. 6. Isosteric heats of adsorption as a function of adsorption coverage.

temperature. When the binding energy is determined from the isosteric heat for low coverage, it can be assumed that the adsorbed gas is only interacting with the substrate and not with other adsorbed atoms [22]. The binding energy of H_2 on FeTi has a value of about 430 J mol^{-1}, at low coverages.

SUMMERY

In this work, adsorption coverage, isosteric heat, and binding energy of H_2 adsorbed on FeTi were reported. Amount of hydrogen adsorption indicates that FeTi has a good hydrogen storage capacity. This alloy has certainly desirable characteristics as an adsorbent due to its isosteric heat of adsorption and binding energy.

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