THEORETICAL ASPECTS OF HYDROGEN STORAGE IN CLATHRATE HYDRATES: LATTICE DYNAMICS AND FIRST-PRINCIPLES CALCULATIONS

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ABSTRACT
In order to accurately estimate the thermodynamic properties of hydrogen hydrates, we developed a method based on the van der Waals and Platteeuw theory of with some modifications that include multiple occupancies, host relaxation, and the description of the quantum nature of hydrogen behavior in the cavities. In this approach we used a combination of lattice dynamics and a first-principles calculation to estimate the free energies, equations of state, and chemical potentials of hydrogen hydrates. Here, we will review our recent activities related to thermodynamic properties and the hydrogen storage amount for pure and binary hydrogen hydrates. First, we have analyzed the formation of hydrogen hydrates stabilized by guest molecules which may also fill small cavities. Second, we have estimated the thermodynamic properties of several hydrate structures that can hypothetically store more hydrogen than the CS-II hydrate.

Keywords: hydrogen storage, clathrate hydrate, phase diagram, binary systems, modeling

INTRODUCTION
The present environmental factors and limited energy resources have led to a profound evolution in the way we view the generation, storage and supply of energy. Therefore, the technological solutions that involve alternative possibilities of energy supply and storage are in urgent need of development. Therefore, research on adequate H-storage materials remains a challenge [1].

The clathrate hydrate is a special class of inclusion compounds consisting of water and guest atoms or molecules. These compounds are formed when water molecules arrange themselves in a cage-like structure around guest molecules and can been considered as material for hydrogen storage application. Such interest has risen after a report that the clathrate hydrate of structure II (CS-II) (see Figure 1) can store around 4.96 wt % of hydrogen at 2200 bar and 234 K [2]. After that, the researchers have concentrated on accurate estimation of the hydrogen capacity of the CS-II clathrate hydrate and have focused on the formation of hydrogen hydrates at lower pressure since the extreme pressure required to stabilize pure hydrogen clathrate hydrates makes it impractical for commercial use [3, 4]. A significant reduction in the hydrate formation