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Hydrogen Adsorption on Type-5 Penta-MgN_8 Sheet, Nanotube, and 3D Porous Structure

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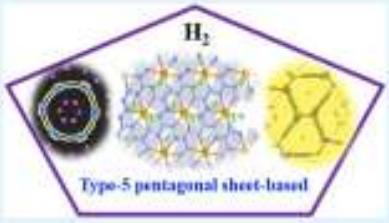
ABSTRACT: Motivated by the recent report on penta-MgN_8 sheet [*Mater. Today Phys.* **2023**, 38, 101259] that is the first realization of type-5 pentagonal 2D tessellation with exposed regularly distributed Mg ions, we carried out density functional theory studies on the interactions of H_2 molecules with 1D penta-nanotube, 2D penta-sheet, and 3D porous structures based on penta-MgN_8. We found that when the penta-MgN_8 sheet is assembled to a 3D porous structure or curved to a nanotube, the bandgap increases from 1.18 to 1.35 and 1.88 eV, and the resulting derivatives are stable dynamically. When H_2 molecules are introduced, the nanotube behaves best in adsorption, where each Mg ion can adsorb three H_2 molecules: two on the outer surface and one on the inner surface. The curved geometry of the nanotube makes the Mg ion on the outer surface more exposed as compared with the situations of the 2D sheet and 3D porous structure, resulting in stronger adsorptions to H_2. The gravimetric capacity (volumetric capacity) is 4.25 wt % (63 g/L) and 4.25 wt % (65 g/L) for the studied penta-sheet and penta-nanotube, and the corresponding desorption temperature is 115 and 162 K at 1 atm pressure, respectively, while for the 3D porous structure, the adsorption performance is poor due to the limited space and the less curvature, leading to strong steric hindrance and less exposed configuration for Mg ions. Moreover, the effects of temperature and pressure on adsorption are also discussed.



KEYWORDS: *penta-sheet, H_2 adsorption, nanotube, penta-sheet-based 3D porous structure, density functional theory*

1. INTRODUCTION

Hydrogen emerges as a fuel for the future due to its high energy output per unit mass, abundance, and zero-carbon feature.[1] The United States Department of Energy (DOE) set three main targeting goals by 2025 for discovering and designing new materials that can offer: (1) a gravimetric density of 5.5 wt %, (2) a volumetric density of 40 g/L, and (3) enabling reversible operation under ambient temperatures and moderate pressures.[2] In order to achieve these goals, materials should be composed of light elements. From this perspective, Mg-based systems are of particular interest. The well-known system is magnesium hydride (MgH_2) with high gravimetric and volumetric hydrogen densities. However, the practical use of MgH_2 for hydrogen storage has been limited due to high operation temperatures and sluggish kinetics, where H is chemically bonded with Mg. For the sake of fast kinetics, quasi-molecular H_2 adsorption is more desirable. To this end, Mg is used to functionalize the material surfaces for enhancing H_2 adsorption. For example, when the pentagonal faces of the B_{80} cage are decorated with Mg atoms, the charge transfer from Mg to the B_{80} cage results in positively charged Mg ions which generate an electric field to polarize H_2 molecules with an adsorption energy of 0.20 eV/H_2.[3] For Mg-functionalized small Mg_2B_n (n = 2−14) clusters, the average energy of H_2 adsorption is calculated to be in the range of 0.13−0.22 eV/H_2.[4] When Mg-decorated C_{60} cages are encapsulated into metal−organic frameworks, the complex system exhibits H_2 adsorption heats of 11 kJ mol^{-1}.[5] For Mg-decorated carbon nitride (g-C_3N_4) monolayer,[6] the H_2 adsorption energy is in the range of 0.25−0.1 eV/H_2. For Mg-decorated tetragonal silicon carbide (t-SiC) sheet, the adsorption energy can reach 0.247 eV/H_2.[7] Moreover, a porous magnesium-based metal−organic framework, Mg-MOF-1 [Mg(3,5-PDC)(H_2O)], was synthesized solvothermally in DMF, in which the open Mg metal sites show selective H_2 adsorption with 0.8 wt % at 77 K.[8] A nanoporous cubic magnesium borohydride γ-$Mg(BH_4)_2$ is found to store hydrogen at twice the density of liquid hydrogen (144 g H_2/L of pore volume) and gravimetric density ~5.0 (wt %) with an adsorption energy of 10.5 kJ mol^{-1}.[9] These research advances clearly demonstrate that the open Mg ions bonded with ligands in materials are activating sites for H_2 adsorption, which can be used as one of the criteria to search for candidates for hydrogen storage materials.

Recently, a novel 2D type-5 penta-MgN_8 has been proposed[10] on the basis of newly synthesized N_{18} macrocycles together with Hückel aromaticity and 18-electron rules. The

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