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Introducing Noble Gas as Space Holder under High Pressure to Design Porous Titanium Carbides with Open Metal Sites for Hydrogen Storage at Near-Ambient Conditions

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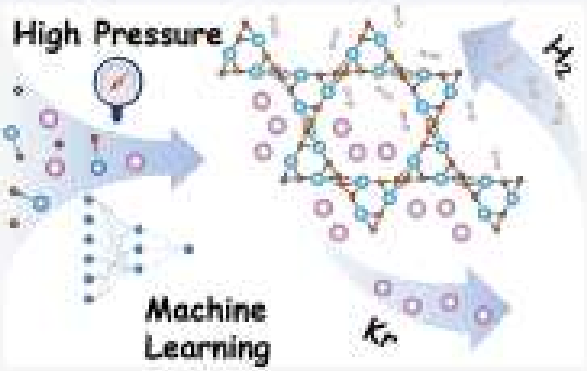
ABSTRACT: It has been a long-standing challenge to develop high-performance solid-state hydrogen storage materials operated under near-ambient conditions. In this work, we propose a new strategy of using noble gases for space holding to design porous titanium carbides with abundant open metal sites for hydrogen storage. By using machine learning and graph theory-assisted universal structure searching methods, we obtain 28 porous titanium carbides from three precursors (TiC dimer, C atom, and Kr atom) under 30 GPa of pressure. The stability and hydrogen storage performance of the resulting structures are further assessed and validated through density function theory and grand canonical Monte Carlo simulations with a DFT-fitted force field. Finally, p-TiC_2 is identified as a promising quasi-molecular hydrogen storage material with capacity of 4.0 wt % and 106.0 g/L at 230 K and 16 bar.



1. INTRODUCTION

Hydrogen energy has been regarded as one of the most promising next-generation energy forms for its high gravimetric energy density, renewability, and zero carbon emissions.[1] However, among the many challenges to realize a clean and efficient hydrogen economy, one main obstacle lies in how to store hydrogen with both high gravimetric and volumetric capacities.[2] The US Department of Energy (DOE) sets a target of storing 5.5 wt % and 40 g/L of hydrogen by 2025, along with an ultimate target requiring 6.5 wt % and 50 g/L of hydrogen stored.[3] The required operating temperature is in the range of −40 to 60 °C. Because of the trade-off between energetics of storage and kinetics of release at near-ambient conditions, the optimal adsorption energy window is within the range of 20 to 80 kJ/mol.[4] Therefore, hydrogen's binding with materials needs to be between physisorption and chemisorption, which can be typically enabled by open metal site (OMS) through Kubas effect[5] and charge polarization effect.[6] The former one is based on transition metal's unfilled d orbital, which receives electrons donated from hydrogen molecule's σ orbital and donates electrons back to the σ^* orbital to form stable complexes, while the latter takes advantages of OMS's local electrical field to polarize H_2 for enhancing the adsorption energy.[7] Different from metal-atom-functionalized porous materials, structures with intrinsic OMSs are much more stable and would not suffer from the clustering problem of metal atoms.[8] Therefore, porous frameworks with abundant ionic OMSs are effective for hydrogen storage. However, in practice, the OMSs in frameworks are hard to control because of two main factors: (1) ligands tend to occupy the OMS in the synthetic process, and (2) the presence of a large amount of OMSs renders materials unstable. Metal organic frameworks (MOFs), as widely explored porous materials,[9−11] typically have very large pore sizes but limited OMSs to adsorb hydrogen near room temperature.[12] Therefore, MOFs can store plentiful hydrogen at cryogenic conditions, but their storage capacity decreases rapidly when the temperature is increased. For instance, NU-1501-Al[13] can store up to 14 wt % and 46.2 g/L of hydrogen at 77 K and 100 bar, while the capacity is reduced to 2.9 wt % and 8.4 g/L at 296 K. Many efforts have been made to increase the density of OMSs in MOFs to improve hydrogen storage capacity at near-ambient conditions. Jaramillo et al.[14] synthesized $V_2Cl_{1.5}$(btdd) that features exposed vanadium(II) sites and can store 1.64 wt % and 10.4 g/L at 298 K and 100 bar. Sengupta et al.[15] recently reported NU-2100 containing robust Cu(I) sites with 32 kJ/mol isosteric heat of adsorption for H_2 that achieves capacity of 10.4 g/L at 233 K and 100 bar. However, how to design porous frameworks containing enough and properly distributed OMSs to store hydrogen under near-ambient conditions remains a grand challenge.

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