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Article

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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assessed and validated through density function theory and grand

canonical Monte Carlo simulations with a DFT-fitted force field. Finally, p-TiC₂ 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 effect⁵ 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.' 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-Al¹³ 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 V₂Cl_{2.8}(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 H₂ 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.

Machine

Learning

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Recently, noble gas clustering in a graphene sandwich has been observed in experiment under near-room-temperature condition.¹⁶ Motivated by this finding, we expect that noble gas atoms can work as a space holder in high-pressure synthesis of porous materials, thus controlling the distribution of the OMSs, as well as the porosity of the materials. Once the pressure is removed, these noble gas atoms are released to form frameworks with micropores and desirable OMSs. On the basis of this idea, we theoretically propose a new strategy by introducing noble gas for space holding under high pressure to get desirable porous structures through global structure search, which are further confirmed by density functional theory (DFT) and DFT-fitted force field grand canonical Monte Carlo (GCMC) simulations, as shown in Figure 1.



Figure 1. Workflow for computational design of porous titanium carbides with intrinsic OMSs via introduction of noble gas.

2. COMPUTATIONAL METHODS

The global structure search under high pressure is performed using machine learning and graph-theory-assisted universal structure searcher (MAGUS),^{17,18} which is accelerated through graph theory.¹⁹ Machine learning potential is used to relax and calculate energies of

structures under an active learning scope, as implemented in MLIP-2 package.²⁰ We run 40 generations to get final porous structures, and each generation contains 150 structures. Between generations, 80% generated structures with low enthalpy act as the seeds for next generation's evolution, while the rest is reconstructed randomly. The void fraction (measuring the probe-occupied volume fraction), surface area, and other structure features are studied with zeo++ package.²¹

The DFT calculations are carried out with the Vienna Ab initio Simulation Package (VASP)²² under the scheme of generalized gradient approximation²³ and projector-augmented wave method.²⁴ The Perdew–Burke–Ernzerhof exchange-correlation functional²⁵ is used along with Grimme's semiempirical DFT-D3(BJ) scheme^{26,27} for the weak interaction between hydrogen and sorbents. The convergence criterion is 10^{-5} eV for the total energy and 0.01 eV/Å for the Hellmann–Feynman force. At this computational level, the equilibrium bond length of the H₂ molecule is 0.75 Å, and its binding energy is 4.54 eV, which are both in good agreement with the experimental results of 0.74 Å and 4.74 eV. The Kubas interaction is analyzed by calculating the crystal orbital Hamilton populations (COHP).²⁸ The phonon calculations are performed with phonopy code.²⁹

The adsorption energy (E_{ads}) of H₂ is computed as

$$E_{\rm ads} = \frac{E_{n\rm H_2} (framework - E_{\rm framework} - n \times E_{\rm H_2})}{n}$$
(1)

where $E_{nH_2@framework}/E_{framework}$ is the total energy of the framework with/without H₂ molecules, E_{H_2} is the energy of one free H₂, and *n* is the number of adsorbed hydrogen molecules.

Hydrogen's gravimetric capacity (G_c) is calculated with

$$G_{\rm c} = \frac{n \times m_{\rm H_2}}{m_{\rm framework} + n \times m_{\rm H_2}} \times 100\%$$
⁽²⁾

where $m_{\rm H_2}$ and $m_{\rm framework}$ are the mass of H₂ and the framework, respectively.

The volumetric capacity (V_c) reads



Figure 2. (a) Schematic diagram of the global structure search to identify porous titanium carbides and (b) landscape of porous TiC_2 structures found with MAGUS in different generations (circles) visualized with the Smooth Overlap of Atomic Positions (SOAP) descriptor under Uniform Manifold Approximation and Projection (UMAP) projection. After optimization with DFT for the structures in the last generation, some (squares) remain porous, while others (triangles) turn into dense configurations. (c) void fraction and (d) surface area versus density of the final 28 porous structures with different compounds.

where $V_{\rm u.c.}$ is the volume of the unit cell.

The desorption temperature (T_d) is calculated via the Van 't Hoff equation,³⁰

$$T_{\rm d} = \frac{|E_{\rm ads}|}{k_{\rm B}} \left[\frac{\Delta S}{R} - \ln P \right]^{-1} \tag{4}$$

where $k_{\rm B}$ is the Boltzmann constant, ΔS stands for the entropy change between gaseous and liquid H₂ (75.44 J/mol·K), *R* is the gas constant, and *P* denotes the equilibrium pressure.

To study the effect of temperature and pressure on storage capacity, grand canonical Monte Carlo (GCMC) simulations are used, where the interaction between hydrogens are modeled with YZ LJ-2S model,^{31,32} while the nonbonded interactions between hydrogen and adsorbent are described with Morse potential fitted with DFT adsorption energies. To sample the potential energy surface of H₂ in *p*-TiC₂, different initial structures are created with one hydrogen molecule placed randomly in a $1 \times 1 \times 2$ supercell of *p*-TiC₂, and each is optimized for 30 steps with framework fixed. A total of 575 configurations are collected to fit the Morse potential between the center of H₂ (denoted as H_{com}) and the framework atom,

$$U_{ij} = \epsilon [(1 - e^{-k(r_{ij} - \sigma)})^2 - 1]$$
(5)

where ϵ and k represent the depth and width of the potential well, respectively; σ is the distance for zero potential; and r_{ij} stands for the distance between particles *i* and *j*.

The GCMC simulations are carried out using RASPA2.0³³ code with 5000 cycles for initialization and 5000 cycles for sampling. Each cycle contains N Monte Carlo moves, including insertion, deletion, translation and rotation, where N is the large value between 20 and the number of hydrogens. All of the atoms in the *p*-TiC₂ framework are fixed in GCMC simulations.

3. RESULTS AND DISCUSSION

3.1. Global Structure Search. Since high pressure can reduce interatomic distance and profoundly modify electron

 Table 1. Lattice Parameters of the Selected Titanium

 Carbides Calculated at Different Pressures

system	pressure (GPa)	a (Å)	b (Å)	c (Å)	volume (Å ³)	space group
Ti ₂ C ₃	30	11.15	10.99	5.53	658.38	Pnnm (58)
	0	11.05	10.94	5.22	631.74	$P2_12_12$ (18)
TiC ₂	30	10.71	10.71	2.81	279.66	$P6_3/m$ (176)
	0	10.99	10.99	2.68	280.70	$P6_3/m$ (176)
Ti_2C_5	30	12.44	11.78	2.78	396.14	Pnnm (58)
	0	12.31	12.04	2.72	403.60	Pnnm (58)
TiC ₃	30	2.66	10.31	7.79	201.01	$P2_{1}/c$ (14)
	0	2.61	12.00	6.94	217.13	Стст (63)

configurations and bonding patterns,³⁴ it is widely used to synthesize novel functional materials.³⁵ Global structure search is an efficient way to computationally determine the stable or metastable structures under high pressure.³⁶ Successful examples include H₃S with a superconducting temperature of 203 K,³⁷ superhard nanotwinned diamond,³⁸ and superionic silica–water/silica–hydrogen compounds,³⁹ which shows that *ab initio* simulations and global structure search play a central role in the discovery of new functional materials under high pressure. Therefore, it can be used to realize our goal of designing porous structures with crystalline OMSs. Equally important, the chemical inertness of noble gas atoms can prevent them from strong interaction with the atoms in the porous framework and can be easily released for getting porous structures. On the basis of these factors, our global structure search consists of three components: (1) transition metal atom Ti as an OMS to adsorb hydrogen, (2) noble gas atom Kr as a space holder, and (3) C atom as the linker to form a substrate because of its well-known flexible bonding feature.

Motivated by the outstanding performance of Ti_2CT_x MXenes for hydrogen storage,⁴⁰ we choose experimentally synthesized TiC dimer⁴¹ as one of the precursors for avoiding the clustering of titanium atoms,⁸ as shown in Figure 2a, where TiC dimer and krypton are first introduced followed by C atoms for global search. No other restrictions are needed in the following process. The stoichiometry is adjusted by changing the components ratio. This global structure search is accelerated with machine learning potential trained on the fly to optimize and predict the energies of the intermediate structures.

We perform eight global structure searches for titanium carbides with five different compositions (TiC, Ti₂C₃, TiC₂, Ti_2C_5 and TiC_3). Each search is composed of 40 generations, and each generation contains 150 structures. Throughout this process, more than 10⁴ structures are computationally screened, while many of them are found to be 2D materials separated by Kr atoms, and less than one-third of structures in each generation have 3D porous morphology. Finally, 104 porous structures are obtained from the last generations. When Kr atoms are removed, 28 different structures are porous after further geometry optimization, as illustrated in Figure S1. For clarity, we select all 3D porous structures in the eight selected generations (5th, 10th, 15th, 20th, 25th, 30th, 35th, and 40th) and calculate their Smooth Overlap of Atomic Positions (SOAP)⁴² descriptor, along with Uniform Manifold Approximation and Projection (UMAP) projection,⁴³ where one point represents one structure, and the distance between two points measures the similarity of corresponding structures. Figure 2b shows the UMAP projection of TiC2 compound for new generated structures, abandoned structures, and inherited structures in different generations. After geometry optimization, some structures remain nearly unchanged, some changed slightly but maintains porous morphology, and some collapse into their dense counterparts. Other UMAP projections for global structure search of TiC, Ti₂C₃, TiC₂, Ti₂C₅ and TiC₃ are given in Figure S2.

The void fractions and surface areas of the final 28 porous structures are in the range of 0.1-0.35 and 10-450 m²/g, as is shown in Figure 2c,d. Such porosity is comparable to that of ambient-condition hydrogen storage materials synthesized in experiments,^{40,44} thereby providing enough adsorption sites and void space for hydrogen adsorption at near-room-temperature.

3.2. Stability of Porous Titanium Carbides. Next, we check the stability of four low-enthalpy structures with different stoichiometry, denoted as p-Ti₂C₃, p-TiC₂, p-Ti₂C₅, and p-TiC₃. As shown in Table 1, the fully relaxed structures change slightly in lattices and volumes after removing the pressure and noble gas atoms to form porous materials with intrinsic OMSs. Especially, p-TiC₂ and p-Ti₂C₅ keep their symmetry unchanged, and the other two undergo geometry deformation with different symmetry but maintain their porosity.



Figure 3. Fully relaxed structures of (a) p-Ti₂C₃, (d) p-TiC₂, (g) p-Ti₂C₅, and (j) p-TiC₃. Phonon dispersion relations of (b) p-Ti₂C₃, (e) p-TiC₂, (h) p-Ti₂C₅, and (k) p-TiC₃. Evolution of potential energies of (c) p-Ti₂C₃, (f) p-TiC₂, (i) p-Ti₂C₅, and (l) p-TiC₃ at zero pressure at 300 and 700 K in 10 ps AIMD simulations.

Table 2. Elastic Constant and Mechanical Properties of p-TiC₂

		el	astic cons	tant (N/m)					
system	C ₁₁	C ₁₂	C ₁₃	C ₃₃	C ₄₄	C ₆₆	bulk modulus (GPa)	Young's modulus (GPa)	shear modulus (GPa)	Poisson's ratio
p-TiC ₂	169.32	81.57	65.76	215.93	31.49	43.87	108.97	116.65	44.13	0.32

The stability can be confirmed with phonon spectra and ab initio molecular dynamics (AIMD) simulations. Using the optimized structure, we calculate the phonon spectra of these four structures, as shown in Figure 3b,e,h,k. They all are dynamically stable given that there is no imaginary part over Brillouin zones. Then, we use a $1 \times 1 \times 2$ supercell for *p*-Ti₂C₃, $1 \times 1 \times 4$ supercell for *p*-TiC₂ and *p*-Ti₂C₅, and $4 \times 1 \times 2$ supercell for *p*-TiC₃ to run AIMD at 300 and 700 K,

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Figure 4. (a) Front view of a $2 \times 2 \times 2 p$ -TiC₂ supercell. Inserts are the basic structure unit and bonding configuration labeled with bond length (in Å) and bond angles (in degree). (b) Spin-polarized band structure and density of state of p-TiC₂.



Figure 5. Adsorption geometry (left panel), charge density difference with an isosurface value of 0.004 e/Å (middle panel), and spin-polarized electron density of state (right panel) for p-TiC₂ loaded with 1 H₂ (a-c) and 1.5 H₂ (d-f) per TiC₂.

Table 3. Average Dihydrogen Bond Length $d_{\rm H}^{\rm ave}$, Average Adsorption Energy per H₂ $E_{\rm ads}$, Desorption Temperature $T_{\rm d}$ under 1.0 Bar, Gravimetric Capacity G_c , and Volumetric Capacity $V_{\rm c}$ of *p*-TiC₂ Loaded with Different Number of Hydrogens

loading (per TiC_2)	$d_{\rm H}^{\rm ave}$ (Å)	$E_{\rm ads}~({\rm eV})$	$T_{\rm d}$ (K)	$G_{\rm c}$ (wt%)	$\nu_{c} (g/L)$
1 H ₂	0.800	-0.355	454	2.7	70.7
1.25 H ₂	0.791	-0.291	372	3.4	88.3
1.5 H ₂	0.793	-0.190	243	4.0	106.0
1.75 H ₂	0.782	-0.116	148	4.7	123.7
2 H ₂	0.799	-0.026	33	5.3	141.3

respectively. After heating for 10 ps with a time step of 1 fs, all of the structures remain almost intact, as shown in Figure S3 for the last snapshots of each simulation, and the potential energies oscillate with small amplitude, as shown in Figure $3c_{f,f,i}$. To exclude the limitation of small lattice in AIMD

Table 4. Fitted Parameters of Morse Potential for Interaction between p-TiC₂ and H₂

term (H _{com} -)	<i>с</i> (К)	k (Å ⁻¹)	σ (Å)
C_1	48.375	0.36317	3.44433
C2	9.082	1.40479	4.27517
Ti	3226.125	3.89326	1.99726

simulations, the thermal stability of p-TiC₂ is further confirmed with a 2 × 2 × 4 supercell containing 288 atoms by machine learning force field accelerated AIMD (see Figure S4). The mechanical stability of p-TiC₂ is also validated by calculating the elastic constants that satisfy all three conditions for hexagonal crystal derived from Born–Huang criteria,⁴⁵ as presented in Table 2. The thermal and dynamical stabilities of p-TiC₂ with Kr atoms under 30 GPa are also verified with the phonon spectrum and AIMD simulation, as shown in Figure S5.



Figure 6. (a) Geometry with two nonequivalent C sites in p-TiC₂. (b) Comparison of DFT energies with the fitted Morse energies and color bar for data density. (c) H₂ excess isotherms for p-TiC₂ at 230, 298, and 330 K calculated with DFT-fitted force field GCMC.

Table 5. Comparison of Hydrogen Storage Capacity with Some $MOFs^{13-15,51,52}$ at Near-Ambient Condition

system	ref	$G_{\rm c}$ (wt %)	$V_{\rm c}~({\rm g/L})$	T (K)	P (bar)
NU-1501-Al	[13]	2.9	8.4	296	100
$V_2Cl_{2.8}(btdd)$	[14]	1.6	11.9	298	100
NU-2100	[15]		10.4	233	100
Ni ₂ (m-dobdc)	[51]	2.0	23.8	198	100
Pt-de-MgMOF	[52]	2.5		433	81
<i>p</i> -TiC ₂	this work	4.0	106.0	230	16

3.3. Performance in Hydrogen Storage of p**-TiC**₂**.** The unique structures of porous titanium carbides with abundant OMSs motivated us to further validate their hydrogen storage capacity with DFT calculations. Here, we primarily discuss the performance of p-TiC₂, and the results for other systems can be found in Figure S6 and Table S1.

As shown in Figure 4a, p-TiC₂ contains hexagon pores with a diameter of 9.72 Å, which form a void fraction of 0.32 and a surface area of 444.8 m²/g. Viewing in another way, the p-TiC₂ can also be considered an assembly of a basic unit consisting of one Ti binding with a TiC_5 ring, as shown in Figure 4a, similar to the ground-state configuration of Ti₈C₁₂ cluster with C_{3v} symmetry^{46,47} where one Ti binds with a C₆ ring but different from the two-dimensional TiC₂ monolayer.⁴⁸ The TiC₅ ring in p-TiC₂ is linked with a graphene-like zigzag honeycomb pattern. Such a structural configuration guarantees that each Ti site in p-TiC₂ is a separately distributed OMS with enough space to adsorb hydrogen. The spin-polarized band structure and density of state are presented in Figure 4b, which show metallicity of p-TiC₂ with a magnetic moment of 1.23 $\mu_{\rm B}$ per unit cell originating from the d orbital of titanium, and each Ti site carries a 0.18 $\mu_{\rm B}$ magnetic moment. The Fermi surfaces of both spin-up and spin-down bands in the Brillouin zone are shown in Figure S7.

When one H₂ molecule is introduced to each Ti site in a $1 \times 1 \times 2$ supercell of *p*-TiC₂, the adsorption energy is found to be -0.355 eV, as shown in Figure 5a. The distance between titanium and the center of H₂ is 1.97 Å, and the H–H bond length is 0.800 Å, suggesting that H₂ molecules are adsorbed by typical Kubas interaction⁵ through charge donation/back donation. It can be further validated with charge density difference in Figure 5b where an obvious charge accumulation is observed between dihydrogen bond and titanium, which suggests a weak bond of Ti–H₂ is formed because of Kubas interaction.⁴⁹ More snapshots of charge density difference in

single unit cell are given in Figure S8 for showing the local structures of adsorption. The electron donation and back donation mechanism in this system can also be seen in average partial COHP of Ti-H and H-H bonds in Figure S9. The spin-polarized partial electron density of state in Figure 5c shows that the σ orbital of H₂ and d orbital of Ti have a weak hybridization induced by Kubas interaction, as seen by the overlapped peak of spin-up electrons at around -0.5 eV.

When further loading H_2 in *p*-TiC₂, more H_2 molecules are adsorbed on the center of the nanopore through charge polarization effect⁶ with dihydrogen bond length around the equilibrium length of 0.76 Å, as is presented in Figure S10. This is due to the steric hindrance between hydrogens in a small-pore framework⁵⁰ driving H_2 to fulfill void space. The adsorption parameters for loading different H_2 numbers are summarized in Table 3. As shown in Figure 5d–f, *p*-TiC₂ has an average adsorption energy of -0.190 eV for hydrogens when adsorbing 1.5 H_2 per TiC₂, which corresponds to a desorption temperature of 243 K at 1 bar according to the Van 't Hoff equation. The weight and volumetric capacity of *p*-TiC₂ loaded with 1.5 H_2 per TiC₂ are 4.0 wt % and 106.0 g/L, respectively.

To better describe *p*-TiC₂'s hydrogen storage performance under temperature and pressure, a force field is fitted from DFT data for GCMC simulations, and the corresponding parameters are given in Table 4. Two nonequavilent carbon sites are labeled as C_1 and C_2 , as is demonstrated in Figure 6a. The fitted Morse potential energies have an R-square of 0.90 and absolute square error of 0.38 kcal/mol (16 meV) compared to DFT adsorption energies (Figure 6b). GCMC calculated excess isotherms in Figure 6c show that a maximum gravimetric capacity of 4.0 wt % is reached at 230 K and 16 bar, which is in good agreement with our DFT outcomes. Moreover, p-TiC₂'s hydrogen storage performance is insensitive to pressure because of the appropriate adsorption energy from Kubas interaction and maintains a capacity of 3.7 wt % at 298 K and 1 bar, thereby showing its promise as a hydrogen storage material in ambient condition.

In addition, some H_2 molecules are also found to be dissociated in *p*-TiC₂ and chemically adsorbed in interstitial void with a binding energy of -1.604 eV per H atom (Figure S11), thereby making the capacity increase to 4.9 wt % and 129.6 g/L, which is nearly two times that of liquid hydrogen at 21 K and 1 bar (71 g/L). For comparison, as listed in Table 5, the gravimetric capacity of quasi-molecular storage in *p*-TiC₂ is close to US DOE's 2025 target, while the volumetric capacity significantly surpasses the target, thereby showing the merits of this new structure.

4. CONCLUSIONS

In summary, using machine learning and graph-theory-assisted universal structure search combined with DFT-fitted force field GCMC simulations, we proposed a new strategy to achieve a controllable design of porous materials with intrinsic OMSs for hydrogen storage under near-ambient conditions. Especially, p-TiC₂ is identified with dynamic stability and thermal stability to exhibit high performance for hydrogen storage with quasimolecular adsorption capacity of 4.0 wt % and 106.0 g/L at near-ambient condition, while the total capacity values become 4.9 wt % and 129.6 g/L when chemisorption is included. Different from the conventional method by modifying the materials surface with doping metal atoms, our strategy can introduce the open metal sites in the intrinsic backbone of porous materials to avoid the clustering problem, and this strategy can be used to design new porous materials not only for hydrogen storage but also for capturing CO₂, CO, N₂, SH₂, and other molecules.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c07772.

Stability, electronic structure, magnetic property, charge analysis, adsorption parameters, and CIF files of the studied structures (PDF)

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Notes

The authors declare no competing financial interest.

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