Assessing the Usefulness of Transition Metal Carbides for Hydrogenation Reactions

Hèctor Prats,^a Juan José Piñero,^a Francesc Viñes, ^{a*} Stefan T. Bromley,^{ab} Ramón Sayós,^a and Francesc Illas^a

^a Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, c/ Martí i Franquès 1-11, 08028 Barcelona, Spain

^b Institució Catalana de Recerca i Estudis Avançats (ICREA), Passeig de Lluís Companys, 23, 08010 Barcelona, Spain

* Corresponding author: francesc.vines@ub.edu

S1. Computational Details

Present details of the periodic Density Functional Theory (DFT) calculations follow the discussion in the main text. The valence electron density was expanded in a plane wave basis set with a kinetic energy cutoff of 415 eV. The effect of core electrons on the valence electron density was taken into account through the Projected Augmented Wave (PAW) method.^{1,2} The employed k-point meshes have been selected by a Monkhorst-Pack scheme,³ and a 9×9×1 mesh was used for all the slab calculations. A separating vacuum region of 10 Å between periodically repeated slabs was found to be sufficient to avoid spurious interactions between the interleaved slabs. The slabs were constructed using the lattice parameter taken from the optimized bulk TMC crystal.⁴ Each slab contains four atomic layers; the two uppermost ones have been allowed to fully relax, whereas the two bottom layers were fixed at optimized bulk crystal positions to simulate the bulk rigidity. To represent the (001) surface of the different TMCs. $(2\sqrt{2} \times 2\sqrt{2})R45^{\circ}$ supercells containing 32 C and 32 M (metal) atoms were used. All surface geometries were optimized before placing any adsorbate. Initial guesses for adsorbate geometries were obtained by placing the adsorbate at different sites. For atomic structure optimizations, the conjugated-gradient algorithm has been employed with an energy convergence criterion for electronic updates of 10⁻⁵ eV, and an atomic force convergence criterion of 0.02 eV Å⁻¹. Final total energies were obtained by extrapolation to 0 K (no smearing). The optimized geometries have been characterized as minima in the potential energy surface by frequency analysis with elements of the Hessian matrix computed as finite differences (0.03 Å displacements) of analytical gradients.

The gas-phase energy for molecular hydrogen, $E_{H_2(g)}$, is calculated by placing the H_2 molecule in an

asymmetric box of $9 \times 10 \times 11$ Å at the Γ -point. Then, the adsorption energy, $\Delta E_{i,ads}$, of either the adsorbed H₂ or the H species is calculated as:

$$\Delta E_{H_{2},ads} = E_{H_{2},slab} - \left(E_{slab} + E_{H_{2}(g)} \right)$$
(1),

$$\Delta E_{H,ads} = E_{H,slab} - \left(E_{slab} + \frac{1}{2}E_{H_2(g)}\right) \tag{2},$$

where $E_{i,slab}$ is the energy of the species *i* adsorbed on the corresponding slab model and E_{slab} is the energy of the relaxed clean slab. With this definition, the more negative the $\Delta E_{i,ads}$ value is, the stronger the adsorption is. Note that the Zero Point Energy (*ZPE*) term is included in all reported energy values.

S2. Optimized Geometries of Adsorbate Species

Figure S1. Optimized geometries (top view) for H_2 , H, and $H_{2,Kubas}$ on all TMCs studied. C and H atoms are shown as grey and white spheres, respectively, whereas M atoms (M = Ti, Zr, Hf, V, Nb, Ta, Mo) are represented by spheres with a different color.



Electronic Supplementary Information (ESI)



S3. Optimized Geometries of Transition States

Figure S2a. Optimized geometries (top view) for the TSs I-III on all studied TMCs. Colour code is as in Figure S1.





Figure S2b. Optimized geometries (top view) for the TSs IV-VI on all studied TMCs. Colour code is as in Figure S1.



Electronic Supplementary Information (ESI)



Figure S2c. Optimized geometries (top view) for the TSs VII and VIII on TaC. Colour code is as in Figure S1.



S4. Energy Profile for TaC

Figure S3. Energy profile (PBE-D3, including ZPE) for the H₂ adsorption, diffusion, desorption, and dissociation on TaC(001) including TSs IV, V, VII, and VIII.



Reaction coordinate

S5. Adsorption Energies without Dispersive Forces

Table S1. Calculated adsorption energy values ($^{\Delta E_{ads}}$) for H₂, H, and H_{2,Kubas} on the (001) surface of the studied TMCs. All values have been obtained using the PBE exchange-correlation functional, and include the ZPE term.

				$\Delta E_{ads} (eV)$			
Site	TiC	ZrC	HfC	VC	NbC	TaC	δ -MoC
$H^{*(top-M)}_{2}$	0.04	0.00	-0.01	0.10	0.03	0.00	-0.27
$H^{*} {(top - C) \choose 2}$	0.03	0.03	0.03	0.06	0.05	0.04	-0.49
$H^{*(top-M)}$	1.77	1.57	1.20	0.88	0.58	0.26	0.46
H * (top – C)	-0.15	-0.26	-0.19	0.46	0.48	0.57	-0.09
$H^{*(top-C)}_{2,Kubas}$	-0.20	-0.36	-0.11	0.41	0.34	0.58	-0.91

S6. Adsorption Energies without Dispersive Forces

Table S2. Calculated H-H bond length, $d(H_2)$, and interaction energy in between both H atoms, $E_{int} - E_{int} = E_{Kubas} - 2 \cdot H_{vac}$ for the obtained $H_{2,Kubas}$ situations on the (001) surface of the studied TMCs. Distances are given in Å and energies in eV, respectively.

TMC	$d(H_2)$	$E_{\rm int}$
TiC	1.73	-0.79
ZrC	1.72	-0.82
HfC	1.72	-0.83
VC	1.69	-0.90
NbC	1.69	-0.92
TaC	1.71	-0.85
δ_{-MoC}	1.80	-0.55

S7. Comparison with Other Materials on the Literature

Table S3. Calculated energy barriers for H₂ dissociation with respect to H_{2(g)} $({}^{H_{2(g)}} \rightarrow {}^{2H})$ on different TMCs and transition metal surfaces. All values except that for Ni(111) include the ZPE term.

Surface	Energy barrier (eV)	Ref.
TiC(001)	0.59	This work
ZrC(001)	0.41	This work
HfC(001)	0.37	This work
VC(001)	0.60	This work
NbC(001)	0.54	This work
TaC(001)	0.34	This work
δ-MoC(001)	~0.00	This work
WC(001)	~0.00	5
Cu(111)	0.47	6
Cu(100)	0.54	6
Cu(211)	0.56	6
Ag(111)	1.03	6
Ag(100)	1.06	6
Ag(211)	1.03	6
Au(111)	0.95	6
Au(100)	0.68	6
Au(211)	0.75	6
Ni(111)	0.13	7
Pt(111)	~0.00	8

REFERENCES

1 P. E. Blöch, Projector Augmented-Wave Method. Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 50, 17953

2 G. Kresse and D. Joubert, From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1999, **59**, 1758

3 H. J. Monkhorst and J. D. Pack, Special Points for Brillouin-Zone Integrations. *Phys. Rev. B: Solid State* 1976, **13**, 5188

4 C. Kunkel, F. Viñes and F. Illas, Transition Metal Carbides as Novel Materials for CO₂ Capture, Storage, and Activation. *Energy Environ. Sci.* 2016, **9**, 141-144

5 A. A. Koverga, E. Flórez, L. Dorkis and J. A. Rodriguez, CO, CO₂ and H₂ Interactions with (0001) and (001) Tungsten Carbide Surfaces: Importance of Carbon and Metal sites. *J. Phys. Chem. C* 2019, **123**, 8871-8883

6 Y. Bai, B. W. J. Chen, G. Peng and M. Mavrikakis, Density Functional Theory Study of Thermodynamic and Kinetic Isotope Effects of H_2/D_2 Dissociative Adsorption on Transition Metals, *Catal. Sci. Technol.* 2018, **8**, 3321-3335.

7 C. Zhi, Q. Wang, B. Wang, D. Li and R. Zhang, Insight into the Mechanism of Methane Synthesis from Syngas on a Ni(111) Surface: a Theoretical Study. *RSC Adv.* 2015, **5**, 66742-66756.

8 L. C. Grabow, A. A: Gokhale, S. T: Evans, J. A. Dumesic and M. Mavrikakis, Mechanism of the Water Gas Shift Reaction on Pt: First Principles, Experiments, and Microkinetic Modeling. *J. Phys. Chem. C* 2008, **112**, 4608-4617.