

COMMUNICATION

Assessing the Usefulness of Transition Metal Carbides for Hydrogenation Reactions

Received 00th August 2019,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

Transition Metal Carbides (TMCs) are proposed to replace scarce and expensive late Transition Metals (TMs) as heterogeneous catalysts, often implying hydrogenation reactions or steps. Present density functional theory based calculations support using group IV TMCs and δ -MoC as viable alternative catalysts to TMs for so, given the moderate exoergicity and affordable reaction step energy barriers.

Transition Metal Carbides (TMCs) have been attracting much interest in the last decades for diverse technological applications in many fields, including heterogeneous catalysis, solid state chemistry, and materials science.^{1–5} A primary reason for this attention is the unique combination of physicochemical properties arising from the different degrees of ionic/covalent/metallic bonding exhibited in TMCs. In addition, some TMCs display catalytic activities similar or even better than those of noble and Pt-group metals⁶ for a considerable number of reactions including alkene hydrogenation,^{4,7} ammonia synthesis *via* the Haber-Bosch process,⁸ the water gas shift reaction,⁹ methanol synthesis from CO₂,¹⁰ fossil fuel refinement,¹¹ and the production of other diverse chemicals compounds.¹² Most of the aforementioned reactions have in common that they imply elementary hydrogenation steps which, to be carried out in an efficient fashion, require highly active and mobile (available) hydrogen atoms to be present on the TMC catalyst surface.

Hence, factors such as the types of hydrogen species and their stabilities play a central role in such hydrogenation reactions, ultimately determining the catalyst performance. Previous literature on the interaction of H₂ on materials point for to the presence of diverse atomically chemisorbed H species,^{3,4} although other studies highlight the stability of molecularly physisorbed H₂,¹³ even surface *Kubas* H₂ structures (*i.e.*, chemisorbed H₂ with an elongated bond),^{14,15} as well as H moieties present in the bulk, placed in defects or at interstitials.¹⁶ This blend of situations seems to back up a rich

adsorptive landscape of H₂ on TMC surfaces, but, regardless of its central role in a plethora of catalyzed reactions, as above stated, the adsorption, desorption, dissociation, *Kubas* formation, and H and H₂ mobilities on TMCs remain hitherto understudied, and so, poorly understood. Note that the present study focuses in heterogeneous catalysis applications, although the results can be of guidance for TMCs utilization as electrocatalysts for the Hydrogen Evolution Reaction (HER).¹⁷

Herein, we supply this necessary and lacking knowledge cornerstone by a thorough Density Functional Theory (DFT) based computational study of the interaction of atomic (H) and molecular (H₂) hydrogen species on seven rocksalt TMCs. Their (001) surface has been considered, as previous studies have already demonstrated that this surface is the most stable.⁶ By considering a very wide range of molecular and atomic adsorption scenarios, we are able to establish the most energetically favorable H₂ adsorption sites and dissociation pathways. The DFT based calculations have been carried out using the Perdew-Burke-Ernzerhof (PBE)¹⁸ exchange-correlation functional with the contribution of dispersion terms added through the D3 approach, as proposed by Grimme *et al.* (PBE-D3).¹⁹ The system total energy has been obtained by self consistently solving the Kohn-Sham equations with the valence electron density expanded in a plane wave basis set of 415 eV of kinetic energy limit, and using periodic slab surface models. The Vienna *Ab Initio* Simulation Package (VASP) code has been used for all the optimizations.²⁰ All other necessary computational details are provided in the Electronic Supplementary Information (ESI). This computational approach has been proven to be accurate when correlating simulations with experimental data on a number of de/hydrogenation reactions and/or interaction of H or H₂ interactions with TMC-based catalysts.^{4,5,21,25,27}

The H₂ dissociation Transition States (TSs) have been located through the Climbing-Image Nudged Elastic Band (CI-NEB) method,²² employing five intermediate images between reactants —initial state— and products —final state. These images were generated using the Atomic Simulation Environment (ASE)²³ and applying the Image Dependent Pair Potential (IDPP) procedure.²⁴ The gained TSs were characterized by frequency analysis ensuring they exhibit only one imaginary frequency. Note that favourable adsorption

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Electronic Supplementary Information (ESI) available: See

DOI: 10.1039/x0xx00000x

energies, ΔE_{ads} , are defined here negative, and, so, the more negative the ΔE_{ads} , the stronger the bonding. All reported energy values include the Zero Point Energy (ZPE) term, with frequencies estimated within the harmonic approximation.

Table 1 Calculated adsorption energy values (ΔE_{ads}) for H_2 , H, and $H_{2,Kubas}$ on the (001) surface of the studied TMCs. All values include the ZPE term.

Site	ΔE_{ads} (eV)						
	TiC	ZrC	HfC	VC	NbC	TaC	δ -MoC
$H_2^{*(top-M)}$	-0.10	-0.11	-0.11	-0.05	-0.06	-0.13	-0.42
$H_2^{*(top-C)}$	-0.05	-0.04	-0.04	-0.04	-0.01	-0.05	-0.60
$H^{*(top-M)}$	1.51	1.33	1.20	0.60	0.35	-0.06	0.21
$H^{*(top-C)}$	-0.52	-0.61	-0.54	0.10	0.18	0.17	-0.55
$H_{2,Kubas}^{*(top-C)}$	-0.40	-0.51	-0.26	0.24	0.26	0.47	-0.98

Table 2 Calculated TS energy barriers for several steps involving adsorbed H_2 and H species on the (001) surface of the studied TMCs. All values are given in eV and include the ZPE term.

Step	Forward (reverse) energy barrier						
	TiC	ZrC	HfC	VC	NbC	TaC	δ -MoC
$H_2^{*(top-M)} \xrightleftharpoons{TS_I} H^{*(top-C)} + H^{*(top-M)}$	0.68 (0.00)	0.52 (0.06)	0.48 (0.06)	0.65 (0.00)	0.60 (0.04)	0.47 (0.11)	0.39 (0.31)
$H^{*(top-C)} + H^{*(top-M)} \xrightleftharpoons{TS_{II}} 2H^{*(top-C)}$	0.10 (1.72)	0.03 (1.60)	0.12 (1.50)	0.14 (0.53)	0.38 (0.52)	—	0.19 (0.95)
$2H^{*(top-C)} \xrightleftharpoons{TS_{III}} H_{2,Kubas}^{*(top-C)}$	1.11 (0.47)	1.42 (0.71)	1.44 (0.63)	0.66 (0.62)	0.82 (0.92)	—	1.07 (0.96)
$H_{2,Kubas}^{*(top-C)} \xrightleftharpoons{TS_{IV}} H^{*(top-C)}$	2.13 (1.78)	2.22 (1.75)	2.17 (1.95)	1.57 (1.85)	1.59 (1.86)	0.40 (0.92)	1.92 (1.53)
$H^{*(top-C)} + H^{*(top-M)} \xrightleftharpoons{TS_V} H_{2,Kubas}^{*(top-C)}$	0.13 (1.11)	0.04 (0.90)	0.12 (0.68)	0.22 (0.58)	0.39 (0.63)	0.45 (0.45)	0.36 (1.01)
$H_2^{*(top-M)} \xrightleftharpoons{TS_{VI}} H_2^{*(top-C)}$	0.06 (0.01)	0.07 (0.00)	0.08 (0.00)	0.01 (0.00)	0.05 (0.00)	0.08 (0.00)	0.00 (0.18)
$H_2^{*(top-M)} \xrightleftharpoons{TS_{VII}} 2H^{*(top-M)}$	—	—	—	—	—	0.82 (0.81)	—
$2H^{*(top-M)} \xrightleftharpoons{TS_{VIII}} H^{*(top-C)} + H^{*(top-M)}$	—	—	—	—	—	0.77 (0.42)	—

The H_2 molecular adsorption on each TMC (001) surface has been exhaustively sampled by considering three molecular conformations on the different high-symmetry, non-equivalent sites over the TMC surfaces. The results show that the H_2 molecule ends up being physisorbed on top of either a surface metal atom (top-M) or a surface C atom (top-C), with top-M being the preferred site in almost all the studied TMCs, see Table 1, yet values range -0.01 to -0.13 eV, thus, mostly due to dispersive forces between H_2 and the TMC surfaces; see ΔE_{ads} gained only at PBE level in Table S1 of the ESI. The δ -MoC behaves different than the other TMCs, with a stronger adsorption of the H_2 molecule on both top-M and top-C adsorption sites, the latter being the most stable one, with an ΔE_{ads} of -0.60 eV. The *Kubas* mode for adsorbed H_2 , previously described in the literature for a number of the here contemplated TMCs,^{14,25-27} corresponds to an almost dissociated H_2 molecular state where both atomic H species are adsorbed on the same C atom, with H_2 bond lengths ranging 1.68 to 1.80 Å, see Table S2 of the ESI, and having a non-negligible interaction between them, estimated to be in between -0.55 to -0.92 eV, see Table S2 of the ESI. The adsorption energies reported on Table 1 show that the formation of the *Kubas* mode is actually thermodynamically favorable on group IV TMCs and δ -MoC, with adsorption energies stronger than those of molecular H_2 adsorption on top-C or top-M, yet *Kubas* H_2 is not thermodynamically favored

on group V TMCs. Interestingly, on TaC and δ -MoC (001) surfaces the *Kubas* H_2 leads to an elevation of the surface carbon atom, resulting in a final structure resembling a CH_2 species adsorbed on a C-vacancy site, see Figure S1 of the ESI. However, the strong interaction of surface C atoms with neighbouring surface metal atoms²⁸ prevents considering the CH_2 group as a carbene-type intermediate. Furthermore, although the formation of such H_2 *Kubas* modes is typically assumed barrierless in the literature,^{14,25-27} we found that it actually involves a high energy barrier, as later discussed. Note that, in order to establish the existence of a *Kubas* formation barrier, one should first indeed find a stable physisorbed H_2 state. However, finding this physisorbed site is elusive and very sensitive to the initial conditions of the geometry optimization; for instance, the H_2 adsorbed on top-C requires an initial guess with the H_2 molecule at least at 1.50 Å above the C atom, and when initial conditions had the H_2 closer to the surface, the adsorption directly evolves to the *Kubas* mode, giving the wrong impression that the process is non-activated. This could well be the reason why this barrier was not found in previous studies in the literature, yet it is crucial for providing a correct description of the ability of TMC surfaces to adsorb and dissociate H_2 , *vide infra*.

The atomic H adsorption was also studied considering six different non-equivalent sites on the TMC surfaces. Results show that, once again, top-M and top-C are the only stable

TMCs. Note also that, on all TMCs except NbC, the $H_{2,Kubas}$ configuration is higher in energy than that for the coadsorption of two H species both on top-C; on NbC the $H_{2,Kubas}$ is 0.10 eV lower. However, it is on δ -MoC that H on top-C position and the H_2 Kubas situation should be regarded as competitive.

In summary, the present work demonstrates that group V TMCs are probably not the best candidates for efficient hydrogenation reactions, given the very low physisorption energies of H_2 and the endoergicity of $H_{2,Kubas}$ formation and of the H_2 dissociation. In fact, for group V, the only dissociated state which is lower in energy than H_2 in the gas-phase is the coadsorption of two H species on two top-M sites in TaC. On the other hand, group IV TMCs are likely to be good candidates to replace noble metals as heterogeneous catalysts for hydrogenation reactions, see comparison of energy barriers in Table S3 in ESI. Although group IV TMCs also exhibit very low H_2 physisorption energies, the adsorption energies for dissociated H states or the $H_{2,Kubas}$ configuration are much stronger. Finally, among the seven studied TMCs, δ -MoC emerges as the best candidate since it exhibits moderate adsorption energy for molecular H_2 , $H_{2,Kubas}$, and atomic H entities, plus features the lowest energy barrier for H_2 dissociation on top-M site. Additionally, our results show that on the group IV TMCs and δ -MoC predicted as good candidates for hydrogenation reactions, the coadsorption of two H species on two separate top-C sites is always preferred compared to the formation of $H_{2,Kubas}$. Moreover, the direct formation of $H_{2,Kubas}$ modes from physisorbed H_2 on top-C is energetically hindered. To summarize, present results show that, for hydrogenation reactions, TMCs can outperform late transition metals featuring comparable or even smaller energy barriers for H_2 dissociation.

Conflicts of interest

There are no conflicts to declare.

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