Structure-activity correlation of Ti$_2$CT$_2$ MXenes for C–H activation

To cite this article: Kaifeng Niu et al 2021 J. Phys.: Condens. Matter 33 235201

View the article online for updates and enhancements.
Structure-activity correlation of Ti$_2$CT$_2$ MXenes for C–H activation

Kaifeng Niu$^{1,2}$, Lifeng Chi$^2,$*, Johanna Rosen$^1$ and Jonas Björk$^{1,*}$

$^1$ Department of Physics, Chemistry and Biology, IFM, Linköping University, 581 83 Linköping, Sweden
$^2$ Institute of Functional Nano & Soft Materials (FUNSOM) and Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou 215123, People’s Republic of China

E-mail: chilf@suda.edu.cn and jonas.bjork@liu.se

Received 22 December 2020, revised 7 February 2021
Accepted for publication 22 February 2021
Published 10 May 2021

Abstract

As a burgeoning class of 2D materials, MXenes have recently attracted significant attention within heterogeneous catalysis for promoting reactions such as hydrogen evolution and C–H activation. However, the catalytic activity of MXenes is highly dependent on the structural configuration including termination groups and their distribution. Therefore, understanding the relation between the structure and the activity is desired for the rational design of MXenes as high-efficient catalysts. Here, we present that the correlation between the structure and activity of Ti$_2$CT$_2$ (T is a combination of O, OH and/or F) MXenes for C–H activation can be linked by a quantitative descriptor: the hydrogen affinity ($E_H$). A linear correlation is observed between the mean hydrogen affinity and the overall ratio of O terminations ($x_O$) in Ti$_2$CT$_2$ MXenes, in which hydrogen affinity increases as the $x_O$ decreases, regardless to the species of termination groups. In addition, the hydrogen affinity is more sensitive to the presence of OH termination than F terminations. Moreover, the linear correlation between the hydrogen affinity and the activity of Ti$_2$CT$_2$ MXenes for C–H activation of both –CH$_3$ and –CH$_2$– groups can be extended to be valid for all three possible termination groups. Such a correlation provides fast prediction of the activity of general Ti$_2$CT$_2$ MXenes, avoiding tedious activation energy calculations. We anticipate that the findings have the potential to accelerate the development of MXenes for heterogeneous catalysis applications.

Keywords: MXenes, heterogeneous catalysis, hydrogen affinity, dehydrogenation, C–H activation

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

Introduction

In the chemical industry, light olefins (C$_1$ to C$_6$) are considered as important building blocks for the synthesis of organic components [1]. Recently, such building blocks have registered a rapid growth on the global trade market due to the wide applications in further polymerization and functionalization [2]. Conventionally, the most common approaches for commercially producing industrial olefins are steam cracking of naphtha and fluid catalytic cracking of heavy oil [3, 4]. Although the recovery rate of light olefins (especially for propylene) from a fluid catalytic cracking unit has increased by 29% in the past decades, the commercial methods for the synthesis of propylene are still not capable for closing the increasing ‘propylene gap’ [5, 6]. Alternatively, a primary route for
the synthesis of light olefins is via the direct C–H activation of natural abundant paraffin that can be easily obtained from shale gas deposits [7, 8]. Generally, the C–H activations for saturated alkanes proceed with the presence of catalysts such as Pt and CrO$_x$ [9–12]. Nevertheless, the dehydrogenation is thermodynamically restricted to rather high temperatures (770 K for 20% conversion of propane) due to the chemical stability of the C–H bond [13]. Such high temperatures and its endothermic nature make the reaction energy-inefficient. Moreover, these catalysts still suffer from limitations including high costs, poor chemoselectivity and toxicity of active centers [14, 15].

In the past decades, various strategies have been employed to improve the catalytic performance of catalysts towards dehydrogenation of alkanes. For example, the selectivity towards propylene can be effectively promoted by alloying another metal (e.g. Sn) into Pt catalysts in the propane dehydrogenation [16]. The underlying mechanism can be ascribed to a geometric effect, in which introduced metal would help generate dispersed Pt active sites [17]. Taking into account that the C–H cleavage would take place on every surface Pt atom, the catalytic performance of the Pt-metal alloy catalysts is still highly structure-sensitive [18]. On the other hand, metal-oxides catalyze the C–H bond activation via the so-called radical-like pathway, in which the M–O sites serve as the active sites [19]. However, due to the structural complexity, the mechanism of M–O sites for C–H activations are elusive [20]. For instance, the activity of the V–O and Cr–O sites are highly sensitive to the bonding nature between the metal ions and O sites [15, 21]. Such diversity of active sites hinders the generation of uniformly dispersed M–O sites with high catalytic activity towards C–H activations [18]. Therefore, it has been long desired to obtain catalysts with uniformly-dispersed active sites and high catalytic performance towards the dehydrogenation of light alkanes.

Two-dimensional materials have been considered as promising catalysts towards various heterogeneous catalysis due to unsaturated and uniformly-distributed active sites [22, 23]. MXenes, with the general formula of $\text{M}_{x}\text{X}_n\text{T}_y$, have attracted tremendous interests in many different fields due to the tunable electronic structure and good thermal stability [24, 25]. Moreover, the O termination groups of MXenes may serve as the active sites for various heterogeneous catalysis [26]. For instance, Jiang et al have reported that the Ti$_3$C$_2$O$_x$ exhibits high catalytic activity towards hydrogen evolution reaction, which is attributed to the highly-active O-sites on the basal plane [27]. Of importance, Diao et al have shown that the Ti$_3$C$_2$O$_x$ MXenes possess remarkable catalytic activity towards the ethylbenzene dehydrogenation [28]. Theoretical calculations reveal that the O termination groups are considered to account for the good catalytic performance. Nevertheless, three possible termination groups (O, OH and F) can be experimentally observed in the MXenes synthesized by HF etching [29]. Previous studies have shown that the co-existence of multiple termination groups are commonly observed via experimental characterization for different MXenes [30, 31]. In addition, properties of MXenes such as electronic properties and catalytic activity are highly dependent on the surface chemistry [32]. For instance, the O termination always increases the work function while the OH termination would decrease it [33]. Furthermore, the configuration and defects of termination groups including O-vacancy not only tune the electronic structure but also enhance the catalytic activity [34]. Therefore, it is crucial to study how termination groups influence the property of MXenes as well as to explore the correlation between the termination configuration and the catalytic performance of the catalyst. Previous studies have shown that the catalytic performance of MXenes is closely related to the ratio of O terminations, in which more O terminations would lead to better catalytic activity [35]. Our preceding study has shown how the hydrogen affinity ($E_H$)—the ability of an O active site to abstract a H atom—could be used to characterize the termination configurations of Ti$_2$CT$_2$ MXenes and the activity towards C–H activations [36]. For the O/OH terminated Ti$_2$C MXenes, the mean hydrogen affinity is linear to the overall ratio of O terminations. Moreover, the hydrogen affinity exhibits linear correlations with respect to the activation energies for C–H cleavage at both –CH$_2$ and –CH$_3$– sites of propane. Note that the dehydrogenation at –CH$_3$– site is energetically favorable, indicating high selectivity of the Ti$_2$CO$_x$(OH)$_{2−x}$ MXenes towards propane dehydrogenation [36]. However, the influence of F terminations on the catalytic activity and selectivity is yet to be addressed, to obtain a complete understanding of the correlation between the termination configurations and the catalytic activity, including O, OH and F terminations.

The main purpose of the present study is to obtain a more complete understanding of the influence of the termination groups on the catalytic activity for the Ti$_3$CT$_2$ MXene; in particular how the F terminations affect the hydrogen affinity of the MXenes, and whether or not the linear correlation between the hydrogen affinity and the catalytic activity is valid for generalized Ti$_2$CT$_2$ MXenes. By performing first-principles calculations, we show that the mean hydrogen affinity of the Ti$_3$CT$_2$ (T = O, OH and F) MXene is linear to the ratio of the O terminations to all terminations present on the surface. The influence of the F termination on the hydrogen affinity is weaker than that of OH termination, i.e. with the same O ratio, the O and F terminated Ti$_3$C possesses lower hydrogen affinity compared to O and OH terminated ones. Furthermore, the catalytic activity of the Ti$_2$CT$_2$ MXene towards C–H activations of propane is investigated. It is found that the validity of probing activity by hydrogen affinity can be extended to all three possible termination groups. Of importance, a universal linear correlation can be found between the activation energies of C–H bond at the –CH$_3$– site and the hydrogen affinity, indicating that the catalytic activity can be solely characterized by the hydrogen affinity.

1. Methods

All density functional theory (DFT) calculations were performed by the Vienna ab initio simulation package together with the atomic simulation environment [37, 38]. The projected augmented wave potentials were employed for describing electron–ion interactions [39]. The exchange–correlation
interactions were treated by van der Waals density functional (vdWDF) with the version of rev-vdWDF2 proposed by Hamada [40]. The energy cutoff for the plane wave was set as 400 eV. A 20 Å vacuum layer was adopted to prevent the periodic image interactions. A combined method of climb-image nudged elastic band (CI-NEB) and dimer method was employed for the search of transition states [41–43]. Firstly, 20 images were generated between the initial and final state. Secondly, the central image was used as the input for the further dimer method in order to obtain the transition state. The structure of local minima and saddle point were optimized until the average atomic force was lower than 0.02 eV Å⁻¹. As illustrated in scheme 1, three types of \(p(4 \times 4)\) supercells of Ti₃CT₂ were employed as catalysts: (a) O/F terminated, (b) O/OH terminated, and (c) a mixture of all three terminations. The calculation of the hydrogen affinity and the dehydrogenation were performed on the top side of the Ti₃CT₂ MXenes (upper panel of scheme 1), while the bottom surface remained unchanged in order to be consistent with our preceding investigation [35]. The Brillouin zone was modelled by gamma-center Monkhorst–Pack scheme, in which the \( \Gamma \) point and \( 4 \times 4 \times 1 \) grid were adopted for geometry optimization and electronic structure calculations, respectively [44].

2. Results and discussion

2.1. Hydrogen affinity for the O and F terminated Ti₂C MXenes

As suggested by our preceding study, the hydrogen affinity \((E_H)\) can be considered as a function of the termination configuration for O/OH terminated Ti₂C. Herein, the validity of the correlation between the \(E_H\) and termination configurations is extended by including F terminations. The hydrogen affinity is defined as the ability of O termination on the top surface for abstracting one H atom from the molecule:

\[
E_H = E\left(\text{M}_m\text{O}_x\text{F}_y\text{H}_{z+1}\right) - E\left(\text{M}_m\text{O}_x\text{F}_y\text{H}_z\right) + \frac{1}{4}E(\text{O}_2) - \frac{1}{2}E(\text{H}_2\text{O})
\]

in which the \(E\left(\text{M}_m\text{O}_x\text{F}_y\text{H}_{z+1}\right)\), \(E\left(\text{M}_m\text{O}_x\text{F}_y\text{H}_z\right)\), \(E(\text{H}_2\text{O})\) and \(E(\text{O}_2)\) are referred to the potential energy of the catalyst with an extra H atom, the original catalyst, a water molecule and an oxygen molecule, respectively [36, 45]. Such descriptor is expected to be related to the termination configuration of the Ti₂C MXenes that can be characterized the by ratio of O terminations to all terminations present on the surface:

\[
x_O = \frac{N_O}{N_O + N_{OH} + N_F}
\]

in which \(N_O\), \(N_{OH}\) and \(N_F\) denote the number of O, OH and F terminations, respectively (\(N_{OH} = 0\) for O/F terminated Ti₂C). It should be noted that the same \(x_O\) may lead to different combination of \(x_{O\text{–top}}\) (the ratio of O terminations to all terminations on the top surface) and \(x_{O\text{–bottom}}\) (the ratio of O terminations to all terminations on the bottom surface). Therefore, five different configurations are considered in order to eliminate the influence of the termination distribution for each combination of \(x_{O\text{–top}}\) and \(x_{O\text{–bottom}}\). Our calculations show that the influence of the termination configuration on the hydrogen affinity is limited, in which the variance is smaller than 0.01 eV for MXenes with the same combination of \(x_{O\text{–top}}\) and \(x_{O\text{–bottom}}\) [as listed in table S1 (https://stacks.iop.org/JPCM/33/235201/mmedia)]. As seen in figure 1, the mean hydrogen affinity is linear to the ratio of O groups \(x_O\) for both O/OH terminated Ti₂C and O/F terminated Ti₂C, in which the higher O ratio leads to lower hydrogen affinity, agreeing well to our previous study [36]. Of importance, the F termination exhibits weaker influence on the hydrogen affinity compared to OH groups. As seen, the distribution of \(E_H\) for the O/F terminated Ti₂C (blue triangles) is lower than that of O/OH terminated Ti₂C (pink triangles). In particular, the mean \(E_H\) for O/F terminated Ti₂C is lower than that of O/OH terminated Ti₂C at the same \(x_O\), indicating that the influence of the F terminations on the hydrogen affinity is not as significant as the OH terminations. Furthermore, the discrepancy between \(E_H\) for O/F terminated Ti₂C and O/OH terminated Ti₂C is increasing as the decreasing of the \(x_O\). Such results indicate that the ability of O terminations to abstract H atoms is more sensitive to the ratio of OH terminations.
Figure 1. The correlation between the hydrogen affinity ($E_H$) and the ratio of the O termination groups of Ti$_2$CT$_2$. The blue and red triangles refer to the hydrogen affinity of Ti$_2$CO$_z$F$_{2-z}$ and the Ti$_2$CO$_z$(OH)$_{2-z}$ (0 ≤ z ≤ 2), in which the blue dots and the red circles represent the mean affinity, respectively. The blue and red lines are the corresponding linear regression of mean $E_H$ with respect to the ratio of O termination.

Figure 2. The linear correlation of $E_H$ with respect to the ratio of the O termination in the Ti$_2$CT$_2$ MXenes. The red and blue points represent the MXenes in which the ratio of F and OH termination is fixed to 50%, respectively.

2.2. The hydrogen affinity for MXenes with mixture of terminations

The co-existence of all possible termination groups is commonly observed in experiments [46]. Therefore, our subsequent analysis is focused on the hydrogen affinity for Ti$_2$C MXenes with O, OH and F terminations. In addition, the termination groups are randomly distributed on the top and bottom surfaces of Ti$_2$C MXenes, and their structure exhibits high degree of freedom including the ratio of termination groups as well as their distribution on both top and bottom side [47]. Thus, it is difficult to obtain every possible structure for Ti$_2$CT$_2$ MXenes. To begin with, the relation between the hydrogen affinity and the termination configurations is investigated by fixing the ratio of one termination group (F or OH) to 50%. As seen, the mean $E_H$ is linear to the ratio of the O termination in the Ti$_2$CT$_2$ (figure 2). The hydrogen affinity is more sensitive to the ratio of OH terminations, in which the range of the mean $E_H$ for Ti$_2$CT$_2$ with the F terminations fixed to 50% is significantly larger than that of Ti$_2$CT$_2$ with 50% of OH terminations. Further calculations have shown that the change of $E_H$ is solely determined by variation of ratio of O termination when $x_F < 50\%$. The scaling relations for Ti$_2$CT$_2$ MXenes with $x_F < 50\%$ are parallel to each other, in which the slopes of the linear regressions are almost the same (figure S1). Such results agree to our discussion above where effect of the F termination on the hydrogen affinity is less significant. Furthermore, it has been reported that the hydrogen affinity can be employed for probing the catalytic activity, in which the low $E_H$ leads to high activity [45]. Therefore, the Ti$_2$C MXenes with F termination may possess high catalytic activity towards C–H activation.

2.3. The correlation between catalytic activity and hydrogen affinity

The hydrogen affinity is an intrinsic property for not only characterizing the termination configuration, but also probing the catalytic activity towards the C–H activations of propane [36]. We begin by studying the thermodynamics of the C–H activations on Ti$_2$CT$_2$ MXenes. Based on the Brønsted–Evans–Polanyi relation, the energy of transition states ($E_a$) is proportional to the reaction energies ($\Delta E$) of the chemical reactions [48–50]. Herein, catalytic activity of 24 O/OH terminated Ti$_2$C and 16 O/F terminated Ti$_2$C is investigated by calculating the reaction energies. As shown in figure 3, the thermodynamics of the C–H activations on Ti$_2$CT$_2$ MXenes can be lumped into a simple linear correlation, in which the reaction energy increases as the hydrogen affinity increases for both –CH$_3$ and –CH$_2$– sites. Note that the hydrogen affinity exhibits different scaling relations with the reaction energy at the –CH$_3$ site (figure 3(a)). Such discrepancy may be related to the steric hindrance of final states of C–H cleavage. The Ti$_2$C MXenes with low O termination exhibit larger strain, in which the formation of the C–O bond would elongate the Ti-O bonds, resulting in higher potential energy (see figure S2). Such distortion of the final states would decrease the accuracy of the linear regression, leading to different scaling relations with respect to different termination configurations. As seen in figure 3(b), however, the O/OH terminated Ti$_2$C and O/F terminated Ti$_2$C can be grouped into one linear regression for the –CH$_2$– site (black line). Such result indicates that the catalytic activity of the terminated Ti$_2$C MXenes can be accurately predicted by the hydrogen affinity. In addition, six Ti$_2$C MXenes with all three possible termination groups are selected to evaluate the accuracy of the prediction (squares in figure 3, data in tables S1–S3). The mean absolute errors (MAE) for the –CH$_3$ and –CH$_2$– sites are 0.19 and 0.12, respectively. Such small MAE indicate that the hydrogen affinity exhibits high accuracy in the prediction the reaction energy for both –CH$_3$ and –CH$_2$– sites.

Furthermore, DFT calculations have shown that the hydrogen affinity can be utilized as a quantitative descriptor for probing the activity of Ti$_2$CT$_2$ MXenes towards the propane dehydrogenation regardless to the termination configuration.
Figure 3. The linear correlations of the reaction energies ($\Delta E$) with respect to the hydrogen affinity ($E_H$) at (a) $-\text{CH}_3$ and (b) $-\text{CH}_2-$ site. The circles, triangles and squares represent the Ti$_2$CO$_z$(OH)$_{2-z}$, Ti$_2$CO$_z$(F)$_{2-z}$, and Ti$_2$C$(T=O, \text{OH and F}, 0 \leq z \leq 2)$, respectively. The color bar from blue to green corresponds to the ratio of O terminations in Ti$_2$CT$_2$ from fully OH and/or F termination (0%) to Ti$_2$CO$_2$.

Figure 4. The scaling relations between the activation energy and the hydrogen affinity at (a) $-\text{CH}_3$ and (b) $-\text{CH}_2-$ in the propane on the Ti$_2$CO$_z$(OH)$_{2-z}$ (circles) and Ti$_2$CO$_z$(F)$_{2-z}$ (triangles). The color bar from blue to green corresponds to the ratio of O groups in Ti$_2$CT$_2$ from fully OH and F termination (0%) to Ti$_2$CO$_2$.

Note that the C–H activation exhibits similar reaction pathways on Ti$_2$CT$_2$ MXenes independent of the termination stoichiometry, in which the reaction initiates at the physisorption of the propane and finalizes at the co-adsorption of the radical and H atom (exemplified in figure S3). Figure 4 summarizes the activation energies for C–H cleavage on 24 O/OH terminated Ti$_2$C and 8 O/F terminated Ti$_2$C MXenes with respect to $E_H$. As seen, there is no significant difference between the linear regression for the O/OH terminated Ti$_2$C and O/F terminated Ti$_2$C MXenes, indicating that the termination configuration would not affect the scaling relation between the catalytic activity and the hydrogen affinity. Moreover, the validity of such scaling correlation can be extended to both $-\text{CH}_3$ and $-\text{CH}_2-$ site, suggesting that the hydrogen affinity is an intrinsic property of Ti$_2$CT$_2$ MXenes. To this end, it is reasonable to extend the application of the hydrogen affinity to the general Ti$_2$CT$_2$ MXenes ($T=O, \text{OH and F}$).

3. Conclusions

In conclusion, the termination configuration and the catalytic activity of the Ti$_2$CT$_2$ ($T=O, \text{OH and F}$) MXenes are investigated by DFT calculations. The termination configuration of the Ti$_2$CT$_2$ MXenes can be characterized by a quantitative descriptor, hydrogen affinity ($E_H$), which is defined as the ability for an O active site to abstract a H atom from the propane.
Our calculations show that the mean hydrogen affinity is linear to the overall O ratio of the Ti$_2$C MXenes, in which high O ratio leads to $E_{H}$. By considering either O/OH or O/F terminated Ti$_2$C MXenes, the $E_{H}$ is more sensitive to the OH termination groups, while the influence of the F termination groups on the $E_{H}$ is less significant. Such result can be further demonstrated by the $E_{H}$ of Ti$_2$CT$_2$ (T = O, OH and F). For the Ti$_2$C MXenes with low F terminations ($x_{F} < 50\%$), the scaling relations between the hydrogen affinity and the O ratio are parallel, indicating that the effect of F termination can be considered as a constant. Of importance, the linear correlation between the hydrogen affinity and the catalytic activity can be extended to the general Ti$_2$CT$_2$ MXenes, in which the low activation energy and/or reaction energy of C–H activation at both –CH$_3$ and –CH$_2$– site of the propane can be found on the surface with low hydrogen affinity.

**Acknowledgments**

We acknowledge the Collaborative Innovation Centre of Suzhou Nano Science & Technology, the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), and the 111 Project. This work was supported by the Swedish Research Council and the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SPO-Mat-LiU No. 2009 00971), the National Natural Science Foundation of China (NSFC, Grant Nos. 21790053, and 51821002) and the Ministry of Science and Technology (2017YFA0205002). Computational resources were allocated at the National Supercomputer Centre, Sweden, allocated by SNIC. JR acknowledges support from the Swedish Foundation for Strategic Research (SSF) for Project Funding (EM16-0004), and from the Knut and Alice Wallenberg (KAW) Foundation for a Fellowship/Scholar Grant.

**Data availability statement**

The data that support the findings of this study are available upon reasonable request from the authors.

**ORCID iDs**

Jonas Björk [https://orcid.org/0000-0002-1345-0006](https://orcid.org/0000-0002-1345-0006)

**References**

[1] Sun K et al 2018 J. Am. Chem. Soc. 140 4820
[2] Yang M-L, Zhu Y-A, Fan C, Sui Z-J, Chen D and Zhou X-G 2011 Phys. Chem. Chem. Phys. 13 3257
[3] Zhao Z-J, Chiu C-c and Gong J 2015 Angew. Chem., Int. Ed. 53 6477
[4] Hakuli A, Kytövä A and Krause A O I 2000 Appl. Catal. A 190 219
[5] Creaser D, Andersson B, Hudgins R R and Silveston P J 1999 Appl. Catal. A 187 147
[6] Bariás O A, Holmen A and Blekkan E A 1996 J. Catal. 158 1
[7] Valcarcel A, Ricart J, Clotet A, Illas F, Markovits A and Minot C 2006 J. Catal. 241 115
[8] Xie Q, Zhang H, Kang J, Cheng J, Zhang Q and Wang Y 2018 ACS Catal. 8 4902
[9] Niu K, Qi Z, Li Y, Lin H and Chi L 2019 J. Phys. Chem. C 123 4969
[10] Zhao Z-J, Wu T, Xiong C, Sun G, Mu R, Zeng L and Gong J 2018 Angew. Chem., Int. Ed. 57 6791
[11] Zhou H et al 2014 J. Catal. 320 52
[12] Yang M-L, Zhu Y-A, Zhou X-G, Sui Z-J and Chen D 2012 ACS Catal. 2 1247
[13] Chen S, Pei C, Sun G, Zhao Z-J and Gong J 2020 Acc. Mater. Res. 1 30
[14] Latimer A A, Aljama H, Kakekhani A, Yoo J S, Kulkarni A, Tsai C, Garcia-Melchor M, Abild-Pedersen F and Nørskov J K 2017 Phys. Chem. Chem. Phys. 19 3575
[15] Liu G, Zhao Z-J, Wu T, Zeng L and Gong J 2016 ACS Catal. 6 5207
[16] Kumar M, Hammer N, Ronning M, Holmen A, Chen D, Walsley J and Oye G 2009 J. Catal. 261 116
[17] Besenbacher F, Chorkendorff I, Clausen B, Hammer B, Molenbroek A, Nørskov J and Stensgaard I 1998 Science 279 1913
[18] Gai L, To C T and Chan K S 2014 Tetrahedron Lett. 55 6373
[19] Li Z and Wu Y 2019 Small 15 e1804736
[20] Naguib M, Kurtoglu M, Presser V, Lu J, Niu J, Heon M, Hultman L, Gogotsi Y and Barsoum M W 2011 Adv. Mater. 23 4248
[21] Seh Z W, Fredrickson K D, Anasori B, Kibsgaard J, Strickler A L, Lukatskaya M R, Gogotsi Y, Jaramillo T F and Vojvodic A 2016 ACS Energy Lett. 1 589
[22] Jiang Y, Sun T, Xie X, Jiang W, Li J, Tian B and Su C 2019 ChemSusChem 12 1368
[23] Zhao J et al 2018 ACS Catal. 8 10051
[24] Hu T, Li Z, Hu M, Wang J, Hu Q, Li Q and Wang X 2017 J. Phys. Chem. C 121 19254
[25] Harris K J, Bagnet M, Naguib M, Barsoum M W and Goward G R 2015 J. Phys. Chem. C 119 13713
[26] Magne D, Mauchamp V, Celérier S, Chartier P and Cabinoc’h T 2016 Phys. Chem. Chem. Phys. 18 30946
[27] Wen Y, Rufford T E, Chen X, Li N, Lyu M, Dai L and Wang L 2017 Nano Energy 38 368
[28] Liu Y, Xiao H and Goduld A W 2016 J. Am. Chem. Soc. 138 15853
[29] Bafekry A, Nguyen C V, Stampfl C, Akgenc B and Ghergherechi M 2020 Phys. Status Solidi 257 2000343
[30] Gao O, O’Mullane A P and Du A 2016 ACS Catal. 7 494
[31] Niu K, Chi L, Rosen J and Björk J 2020 Phys. Chem. Chem. Phys. 22 18622
[32] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[33] Larsen A H et al 2017 J. Phys.: Condens. Matter 29 237002
[34] Blochl P E 1994 Phys. Rev. B 50 17953
[35] Hamada I 2014 Phys. Rev. B 89 121103
[36] Henkelman G and Jónsson H 1999 J. Chem. Phys. 111 7010
[37] Heyden A, Bell A T and Keil F J 2005 J. Chem. Phys. 122 224101
[38] Henkelman G, Uberuaga B P and Jónsson H 2000 J. Chem. Phys. 113 9901
[39] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188
[40] Latimer A A, Kulkarni A R, Aljama H, Montoya J H, Yoo J S, Tsai C, Abild-Pedersen F, Studt F and Nørskov J K 2017 Nat. Mater. 16 225
[41] Agresti A et al 2019 Nat. Mater. 18 1228
[47] Naguib M, Mochalin V N, Barsoum M W and Gogotsi Y 2014 Adv. Mater. 26 992
[48] Bligaard T, Nørskov J K, Dahl S, Matthiesen J, Christensen C H and Sehested J 2004 J. Catal. 224 206
[49] Cheng J, Hu P, Ellis P, French S, Kelly G and Lok C M 2008 J. Phys. Chem. C 112 1308
[50] Viñes F, Vojvodic A, Abild-Pedersen F and Illas F 2013 J. Phys. Chem. C 117 4168