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C-H activation of light alkanes on MXenes predicted by hydrogen affinity

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Abstract: C-H activation of light alkanes is one of the most important reactions for a plethora of applications but requires catalysts to operate at feasible conditions. MXenes, a new group of two-dimensional materials, have shown great promise as heterogeneous catalysts for several applications. However, the catalytic activity of MXenes depends on the type and distribution of termination groups. Theoretically, it is desired to search for a relation between the catalytic activity and the termination configuration by employing a simple descriptor in order to avoid tedious activation energy calculations. Here, we show that MXenes are promising for splitting C-H bonds of light alkanes. Furthermore, we present how a quantitative descriptor – the hydrogen affinity – can be used to characterize the termination configuration of Ti2CTz (T = O, OH) MXenes, as well as the catalytic activity towards dehydrogenation reactions, using propane as model system. First-principles calculations reveal that the hydrogen affinity can be considered as an intrinsic property of O and OH terminated Ti2C MXenes, in which the mean hydrogen affinity for the terminated Ti2C MXenes is linearly correlated to the statistical average of their OH fraction. In addition, the C-H activation energies exhibit a strong scaling relationship to the hydrogen affinity. This quantity can therefore yield quick predictions of catalytic activity of terminated Ti2C MXenes towards C-H activations, and even predict their chemical selectivity toward scissoring different C-H bonds. We believe that the hydrogen affinity will accelerate the discovery of further applications of the broad family of MXenes in heterogeneous catalysis.
1. Introduction

Light alkanes (C\textsubscript{1} to C\textsubscript{6}) are the principal components in petroleum, natural gas and have been widely used as building blocks for the synthesis of plastics, medicines and chemical components.\textsuperscript{1-3} For instance, the production of olefins via direct C-H activations of light alkanes has been considered as a profitable strategy to satisfy the fast growing demand of olefins in the past several decades.\textsuperscript{4} Furthermore, it has been long desired to achieve further reactions, e.g. polymerization and cyclodehydrogenation, via direct C-H activations of light hydrocarbons.\textsuperscript{5,6} Due to the chemical stability of C-H bonds, however, such activations not only require high energy input, but also depend on catalysts with high efficiency.\textsuperscript{7} Various strategies have been developed to activate C-H bonds under mild conditions by employing noble metals such as Pt, Pd and Ru.\textsuperscript{8-10} Nevertheless, the practical challenge remains in the poor chemoselectivity of C-H activations. Such drawback leads both to low yield and a rapid deactivation due to quenching of active sites by side-products. Conventionally, the efficiency of C-H activations can be increased by applying geometric confinements, e.g. reconstructed metal surfaces with grooves, or alloying catalysts with a different metal to create discrete active sites.\textsuperscript{11,12} For example, alloyed Pt-Sn catalysts have been widely used for achieving the selective dehydrogenations of propane with high efficiency, in which the over-dehydrogenation process would be effectively prevented due to the presence of Sn atoms.\textsuperscript{13-15} Despite this, C-H activations still suffer from obstacles such as high cost and fast deactivation, which can be ascribed to the difficulty in generating catalysts with desired active sites.\textsuperscript{16}

Alternatively, two-dimensional (2D) materials, including metal-organic frameworks and metal anchored CN monolayers, have been demonstrated to possess high activity as heterogeneous catalysts due to low-coordinated and uniformly-distributed active sites.\textsuperscript{17,18} In particular, MXenes, a burgeoning class of 2D materials,\textsuperscript{19} are of considerable interests in many aspects including energy storage, nanoelectronics and catalysis owing to high surface area, tunable electronic structure and good thermal stability.\textsuperscript{20,21} MXenes, originated from so called MAX phases,\textsuperscript{22} are of the general formula M\textsubscript{n+1}X\textsubscript{n}T\textsubscript{z}, where M is a transition metal, X is C and/or N, n equals 1-3, and T represents surface termination groups. Previous studies have shown that O terminated MXenes not only exhibit significant properties but also serve as the support surface in anchoring single-atom active sites.\textsuperscript{23,24} For instance, the 2D molybdenum MXene (Mo\textsubscript{2}CT\textsubscript{2}, T = O, OH and F) exhibit a distinguished catalytic activity towards hydrogen evolution reaction (HER) with an initial overpotential of 283 mV.\textsuperscript{25} Theoretical calculations have shown that such high activity can be ascribed to O terminal groups on the MXene serving as active sites. However, the catalytic activity of MXenes are profoundly influenced by the termination group distribution.\textsuperscript{21} Gao et. al. have theoretically predicted that the catalytic activity of the terminated MXenes (V\textsubscript{2}C, Ti\textsubscript{2}C and Ti\textsubscript{3}C\textsubscript{2} etc.) towards HER can be tuned by achieving different stoichiometric ratios of O and OH terminal groups.\textsuperscript{26} Such tunable terminations of MXenes can be achieved by changing the preparation and/or post processing method.\textsuperscript{27} Moreover, O-containing groups are demonstrated to be active sites for dehydrogenations on MAX phase catalysts.\textsuperscript{28} Recently, Liu and co-works have experimentally achieved the dehydrogenation of ethylbenzene on the fully O terminated Ti\textsubscript{3}C\textsubscript{2} MXene, in which the reactivity of the Ti\textsubscript{3}C\textsubscript{2} MXene is much higher than that of graphene and nanodiamond.\textsuperscript{29} Hence, fully O terminated MXenes are promising as catalysts for dehydrogenations of light alkanes. Furthermore, as OH terminations are a natural consequence of dehydrogenation, their influence is inevitable for such reaction protocols. Therefore, the influence of OH termination on the catalytic activity for MXenes still need to be stressed.

Mechanistically, the C-H activation on an oxygen-promoted catalyst occurs via either the catalyst-stabilized or the radical-like pathway.\textsuperscript{30} In the first, the dissociated C radicals are stabilized by chemisorption on the catalytic surface, resulting in the co-adsorption of the dissociated H atoms and...
C radicals (H(ad) + CnH2n+1(ad)). In the second, however, the radical-like intermediate is stabilized by the formation of OH bond instead of the interactions between the C atom in the radical and the active site, leading to the final state of the reaction as H(ad) + CnH2n+1(g). As a consequence, the transition state (TS) energies for various pathways are distinctly different. The TS energy is often characterized by the scaling relationship of chemical reactions – the Brønsted–Evans–Polanyi (BEP) relation – in which the energy of transition state is proportional to the corresponding reaction energy.
image interactions were avoided by employing a vacuum layer of 20 Å. The transition states search for C-H activations was first calculated with Climbing Image Nudge Elastic Band (CI-NEB), in which 10 images were inserted between initial and final states.48,49 The central images were then used as the input of the Dimer calculations to obtain accurate transition states.50 The structure of all local minima and saddle points were optimized until the average atomic force was below 0.02 eV/Å. The p(4 × 4) Ti2C MXene supercells with O and OH terminal groups were employed as the catalysts, in which the dehydrogenations and the calculations for hydrogen affinity were performed on the top side of MXenes, while the bottom side remained unchanged. The lattice parameter for O terminated Ti2C MXenes (Ti2CO2) was optimized to 3.018 Å. The Brillouin zone of the reciprocal lattice was modeled by gamma-centered Monkhorst-Pack scheme, in which the Γ point and 4 × 4 × 1 grid were adopted for all calculations.51

3. Results and Discussion

To explore the pathway of propane dehydrogenation, we choose fully O terminated Ti2C MXenes (Ti2CO2) as first model system. Herein, the reactions are considered to take place on the one side of the terminated Ti2C MXenes, which is defined as the top side. As shown in Figure 1, the dehydrogenation of the propane on the Ti2CO2 MXene consists of two elementary steps, the C-H activation and the drift of the abstracted H atom. First, the intact propane molecule physisorbs on the top side of the Ti2CO2 (IS). There are then two possible ways the reaction can be initiated: dehydrogenation on the terminal methyl group (-CH3, blue curve) and dehydrogenation on the methylene group (-CH2-, red curve). The C-H activations at both methyl and methylene groups exhibit a radical-like pathway, in which the dehydrogenated radical (C3H7) at the transition state (TS1) is stabilized by the formation of the OH group (TS1 in Figure 1).41 At TS1, the C-H bond lengths are elongated to 2.36 Å and 2.14 Å at the methyl and methylene group, respectively. The activation energy of the respective C-H activations is defined as

\[ E_a = E_{TS1} - E_{IS}, \]  

where \( E_{TS1} \) and \( E_{IS} \) are the total energies of TS1 and IS, respectively. Despite the similarity of reaction pathways for activating C-H bonds, the Ti2CO2 exhibits different catalytic activities towards C-H activations at various hydrocarbon groups, in which the C-H bond scission at the -CH2- group is more energetically favorable with an activation energy (\( E_a \)) of 1.59 eV while the activation energy is 2.01 eV at the -CH3 site. Such barrier indicates that the O-terminated MXene exhibits comparable activity towards C-H activations with transition metal catalysts (Pt-Sn alloy).12 Passing through TS1, the dehydrogenated radical and the dissociated H atom co-adsorb at one O atom of the Ti2CO2 (IM). (We also considered the adsorption of the proxyl radical chemisorbed to the metal site which, however, relaxes into the preferred adsorption to the O atom.) Electronic structure analysis shows that the C-O bonds are formed at the transition complexes, in which electrons are donated from C atoms to the O active sites. In addition, the chemoselectivity of the Ti2CO2 towards different C sites of the propane can be ascribed to the stability of the transition complexes. The transition complex of the CH3 site exhibits stronger interaction with the Ti2CO2 catalyst, leading to a lower activation energy (Figure S1). Subsequently, the dissociated H atom would diffuse to the adjacent O atom with barriers of 0.15 eV and 0.17 eV for -CH3 and -CH2- site, respectively (TS2), which agrees to the previous result on Ti2C2O2.29 Following the dehydrogenation of the -CH2- site, the resulting 2-proxyl radical, adsorbed on the surface, may either undergo a second C-H activation of the same C atom or of one of the terminal -CH3 sites resulting in propylene. Our calculations show that the former reaction has an activation energy of 2.00 eV, while it is just 1.35 eV for the latter. I.e. Ti2CO2 exhibits a strong selectivity towards the synthesis...
of propylene (Figure S2). Notably, the first dehydrogenation step, with a barrier of 1.59 eV, is the rate-limiting step for the overall propylene synthesis. Such reaction pathway with relatively low activation energy shows that the O terminated Ti$_2$C MXenes are promising catalysts in achieving high-efficiency C-H activations. However, post synthesis processing is required to generate the fully O terminated Ti$_2$C MXenes, and the termination groups distribution is highly dependent on the etching methods. Furthermore, as dehydrogenation reactions proceed, an initially fully O terminated MXene will unavoidably incorporate OH terminations. Therefore, a systematic investigation on the catalytic activities of the Ti$_2$C MXenes with various termination groups is needed.

![Reaction pathways for dehydrogenation](image)

**Figure 1.** The reaction pathways for dehydrogenation of (a) the -CH$_3$ and (c) -CH$_2$- group of propane on the top side of the O terminated Ti$_2$C MXene (Ti$_2$CO$_2$), with (b) the corresponding energy profiles. The blue and red curve represent the energy profiles of the C-H activation at the -CH$_3$ group and the -CH$_2$- group, respectively. The C, Ti, O and H atoms are represented by brown, silver, red and white circles, respectively.

Experimentally, the most common termination groups for MXenes synthesized by HF etching from MAX phases are O, OH and F groups, in which the O termination groups are presumed to be active sites for C-H activations. However, the co-existence of the O and OH terminations is inevitable as the dehydrogenations proceed. Therefore, the regeneration of the O active site from OH groups plays a crucial role in the catalytic performance. Different pathways for removing H atoms were considered, as well as the desorption of H$_2$O (Figure S3). The energetically most favored pathway includes the conversion of two adjacent OH groups into H$_2$O and the concomitant associative desorption of H$_2$, with an effective barrier of 1.90 eV and desorption energy of 0.34 eV. The H$_2$O may also desorb as an intact molecule, but the overall desorption energy of such a process is 2.09 eV, i.e. less likely than the H$_2$ desorption. The results agree to experimental observations in which OH can be converted into O terminations by heating or an Ar$^+$ beam. However, we cannot exclude the possibility of H$_2$O
desorption, which could be of importance to consider when rejuvenating the catalytic properties of
the MXene surface for example by heating.

The co-existence of the O and OH groups on Ti$_2$C MXenes is commonly observed, and the relative
fraction between O and OH groups is naturally the most sensitive characteristics of the MXene
termination group configuration during C-H activation. Therefore, we focus on carefully studying how
the OH fraction influences the reactivity. We constructed Ti$_2$CO$_{2-z}$(OH)$_z$ MXenes and selected 24
surfaces with different terminal group distribution and/or stoichiometry to study the catalytic activity
towards C-H activations. In the field of heterogeneous catalysis, the trend of chemical reactions are
often quantitatively characterized by the BEP relation, which has been considered as a useful tool to
predict the kinetic behavior of a chemical reaction based on thermodynamic data. In the context of
C-H activations, the change of the enthalpy can be directly denoted by the reaction energy, the energy
difference between the final and initial states. Considering that the C-H scission process (IS to IM in
Figure 1) is the rate-limiting step in the propane dehydrogenation, the corresponding reaction energy
is therefore defined as:

\[ \Delta E = E_{IM} - E_{IS}, \]

where \( E_{IM} \) and \( E_{IS} \) are the total energies of IM and IS, respectively. Such reaction energies are
calculated to correlate the catalytic activity of MXenes with different termination groups. Figure 2
shows the linear correlation between the reaction and activation energies, in which the C-H activation
at the -CH$_3$ and -CH$_2$- groups can be lumped into separate BEP relations. As seen, the activation energy
exhibits a strong proportional correlation with the corresponding reaction energy, suggesting that the
catalytic activity decreases as the energy of IM increases with respect to that of IS. These results agree
well with elementary reactions at metal surfaces. Despite that the BEP relation has been proved
applicable for C-H activations on the OH and O terminated Ti$_2$C MXenes, the prediction and
characterization of the activity is still limited by the difficulty in optimizing the initial and final states
for a reaction. In addition, outliers in the BEP relation are observed at the surface with the highest OH
ratio on the top side. Such outliers can be ascribed to a steric hindrance that increases the energy of
the transition states. Thus, it is useful to examine the implications of accurately predicting C-H
activation energies with an intuitive and more efficient descriptor.
The fraction of OH groups ($x_{\text{OH}}$), on the other hand, as one of the intrinsic properties of the terminated MXenes, can be directly assessed from post analysis after the synthesis. Here, the $x_{\text{OH}}$ is defined by the ratio of OH groups to all termination groups:

$$x_{\text{OH}} = \frac{N_{\text{OH}}}{(N_{\text{OH}} + N_{\text{O}})},$$

in which the $N_{\text{OH}}$ and $N_{\text{O}}$ denote the number of OH groups and O groups in the MXene, respectively. Previous theoretical studies have shown that it is possible to use the $x_{\text{OH}}$ to characterize the catalytic activity of the MXenes, in which the low $x_{\text{OH}}$ would effectively promote the catalytic activity. Nevertheless, DFT calculations show that such a simple descriptor is not sufficient to quantitatively describe the activity of Ti$_2$CT$_2$ MXenes. The reaction energies of C-H activations at the -CH$_3$ and -CH$_2$- groups are significantly influenced by the fraction of the OH group in Ti$_2$CO$_2$(OH)$_z$ MXenes, in which the barriers for the C-H bond scission are strongly varied as the fraction of OH changes (see Table S1 in the Supporting Information). Nevertheless, there is no obvious trend between the catalytic activity of Ti$_2$CO$_2$(OH)$_z$ MXenes and this quantity. A high fraction of OH groups does not always lead to poor catalytic activity for C-H splitting and a low fraction of OH does not always result in good activity (Table S1). Moreover, such simple model fails to distinguish the activity of Ti$_2$CO$_2$(OH)$_z$ MXenes with the same amount of OH termination groups but different configurations. For example, the reaction energies for the dehydrogenation of the methyl group on the Ti$_2$CO$_2$(OH)$_z$ MXenes with 50% of OH groups are found within a range of 3 eV, suggesting that the fraction of OH is not the main determining factor of the catalytic activities. Instead, we found that the hydrogen affinity is a more suitable quantity to connect the configuration and reactivity of a MXene surface.

The hydrogen affinity ($E_{\text{H}}$) represents the ability of an oxide species to abstract an H atom, defined as

$$E_{\text{H}} = E(M_{\text{m}}O_{\text{x}}H_{y+1}) - E(M_{\text{m}}O_{\text{x}}H_{y}) + \frac{1}{2}E(O_2) - \frac{1}{2}E(H_2O),$$

where the $E(M_{\text{m}}O_{\text{x}}H_{y+1})$, $E(M_{\text{m}}O_{\text{x}}H_{y})$, $E(H_2O)$ and $E(O_2)$ 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 (detailed definition is shown in SI). Such descriptor has been successfully utilized to predict the catalytic activities of O promoted catalysts towards the C-H and C-O activations, in which the catalytic activity decreases as the $E_{\text{H}}$ increases. Based on the definition, the $E_{\text{H}}$ of Ti$_2$CO$_2$(OH)$_z$ MXenes can be influenced by several factors: the overall fraction of OH groups ($x_{\text{OH}}$), the configuration of the termination groups and the adsorption site of the H atom. However, DFT calculations show that the difference between $E_{\text{H}}$ values between different sites for a Ti$_2$CO$_2$(OH)$_z$ MXene with a specific termination configuration is negligible (Table S2). Therefore, subsequent investigations focus on the correlation between the $E_{\text{H}}$ and the distribution of the termination groups.

The termination configuration of MXenes are determined by three dimensions: the fraction of OH groups on the top ($x_{\text{OH}}$-top), the fraction of OH groups on the bottom ($x_{\text{OH}}$-bottom) and the distributions of the OH groups on both sides of the MXenes. In our case, the top side of the MXene is defined as the surface where the H adsorption and reactions take place. The definition of $x_{\text{OH}}$-top and $x_{\text{OH}}$-bottom follows eq. (3), by only considering the number of termination groups on each side of the MXene. Subsequently, the hydrogen affinity of Ti$_2$CO$_2$(OH)$_z$ MXenes with all possible $x_{\text{OH}}$-top and $x_{\text{OH}}$-bottom is calculated.
$x_{\text{OH} - \text{bottom}}$ combinations are investigated. For each combination, 10 structures with different termination group distribution were considered, resulting in a number of 2762 different Ti$_2$CO$_{2-z}$(OH)$_z$ MXenes. Figure 3 shows the hydrogen affinity as a function of the average OH-fraction on both top and bottom of the MXene. The formation of the OH group on all terminated Ti$_2$C MXenes are endothermic ($E_H > 0$ eV), indicating that O terminal groups are more stable than OH terminal groups. Statistically, the mean $E_H$ for Ti$_2$CO$_{2-z}$(OH)$_z$ MXenes exhibits a good linear relation with the fraction of OH groups. Such generalized relation indicates that the $E_H$ can be used to characterize the termination configuration of the terminated Ti$_2$C MXenes. Of importance, the $E_H$ is strongly influenced by the distribution of termination groups. As seen in Figure 3, the standard deviation for the hydrogen affinity at each overall OH fraction is relatively large (grey lines). For instance, the range of $E_H$ is larger than 1.50 eV for Ti$_2$CO(OH) MXenes (the fraction of OH is 50%). Such significant deviation suggests the hydrogen affinity is determined by not only the overall fraction of OH groups but also the termination group distribution.

![Figure 3](image-url)

**Figure 3.** The correlation between the hydrogen affinity ($E_H$) and the fraction of OH groups of Ti$_2$CO$_{2-z}$(OH)$_z$ MXenes ($x_{\text{OH}}$). Grey points represent the $E_H$ values for each Ti$_2$CO$_{2-z}$(OH)$_z$. Blue dots with vertical lines represent the mean $E_H$ for each fraction of OH groups with the standard deviation. The blue line is the linear regression of the mean $E_H$ with respect to the fraction of OH groups.

Further analysis shows that the hydrogen affinity can be considered as an intrinsic property of the termination configuration of Ti$_2$C MXenes. Note that the smallest $E_H$ (0.53 eV) and the largest $E_H$ (2.04 eV) can be found at the Ti$_2$CO$_{2-z}$(OH)$_z$ MXene with the same fraction of OH groups ($x_{\text{OH}} = 43.75\%$) with different configurations of termination groups, suggesting that the hydrogen affinity is determined by the termination groups distribution. Specifically, the fraction of OH groups on the top ($x_{\text{OH} - \text{top}}$) plays an important role in determining the hydrogen affinity. For instance, the MXene with the lowest $x_{\text{OH} - \text{top}}$ and the highest $x_{\text{OH} - \text{bottom}}$ combination possesses the smallest $E_H$, while the Ti$_2$CO$_{2-z}$(OH)$_z$ with highest $x_{\text{OH} - \text{top}}$ and lowest $x_{\text{OH} - \text{bottom}}$ exhibits the largest hydrogen affinity (detailed relation between $E_H$ and termination groups distribution is extracted in Figure S5). Such result indicates that the hydrogen affinity can be used for distinguishing the catalytic activities of MXenes with the same amount of OH groups.

Of importance, the hydrogen affinity can not only represent the termination configuration of Ti$_2$CO$_{2-z}$(OH)$_z$ MXenes but also characterize the catalytic activity of the active sites on the top side. First
of all, the reaction energies for C-H activations of both the -CH$_3$ and -CH$_2$- groups of propane on Ti$_2$CO$_2$(OH)$_z$ MXenes have linear relationships with their corresponding hydrogen affinities (Figure S6). Based on the BEP relation, the activation energies depend linearly on the reaction energies (vide supra). Therefore, the activation energies would increase as the hydrogen affinity increases. As expected, the catalytic activity of Ti$_2$CO$_{2-z}$(OH)$_z$ MXenes towards C-H activations increases as the hydrogen affinity approaches to 0 eV for both the -CH$_3$ and -CH$_2$- groups (Figure 4). Such trends agree well with previous studies, where the catalytic activity towards oxidative dehydrogenation of cyclohexane on Co$_3$O$_4$ nanoparticles can be promoted by reducing the hydrogen affinity of active sites. In addition, the highest activation energies for both C-H activations are obtained on the MXene possessing the highest $E_H$ (2.04 eV) with a stoichiometry of O and OH groups as Ti$_2$CO$_{1.125}$(OH)$_{0.875}$. The underlying mechanism of the poor activity can be ascribed to limited number active sites on the top side to proceed the C-H activations ($x_{OH-top}$ = 87.5% from Figure S6). Therefore, the catalytic activity of the MXenes with the same fraction of OH groups but different distribution can be significantly different. Notably, both the reaction and activation energies are described by a linear relationship with respect to the hydrogen affinity. Thus, simply by calculating the hydrogen affinity of a MXene it is possible to quantitatively assess its activity towards dehydrogenation, within an error margin.

From the trends in Figure 4, it is revealed that the MXenes with low hydrogen affinity ($E_H < 1.0$ eV) exhibit higher activity towards activating the CH$_2$ group than that of CH$_3$ group. The difference in activation energies (> 0.20 eV) is even larger than that of noble metal catalysts (e.g. Pt/Sn alloy). Such distinction in the activity implies that O and OH terminated MXenes have a great potential to be good catalysts for the high-selective catalysts for further functionalization of light hydrocarbons.

4. Conclusions
In conclusion, C-H activations of propane on Ti$_2$CO$_{2-x}$(OH)$_z$ MXenes have been investigated based on DFT calculations. The Ti$_2$CO$_2$ MXene exhibits high catalytic activity towards the C-H activations and the co-existence of multiple termination groups is one of the most vital factors for predicting the catalytic activity. In particular, we propose the hydrogen affinity ($E_H$) as a quantitative descriptor both for characterizing the termination configuration and probing the catalytic activity and selectivity of the Ti$_2$CO$_{2-z}$(OH)$_z$ MXenes, which is not possible by models based purely on thermodynamics or chemical composition. The mean affinity of the overall OH fraction increases as the OH fraction approaches 100%, indicating that Ti$_2$C MXenes with fewer OH terminations are more likely to abstract an H atom from the reactant. Further analysis shows that the catalytic activity is linearly correlated with the hydrogen affinity, in which highly active MXenes possess low hydrogen affinity. It is anticipated that the hydrogen affinity can serve as a theoretical descriptor for efficient evaluation of catalytic activities of terminated Ti$_2$C MXenes and pave the way for the rational design of MXenes based catalysts in general.

Declaration of Competing Interest
The authors declare no competing financial interest.

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Supporting Information
Details of reaction energies and energy barriers of C-H activations on Ti$_2$CO$_{2-x}$(OH)$_z$ MXenes. The catalytic origin of the C-H activations at different sites. The reaction pathways for the re-generation of the O active site. The detailed definition of hydrogen affinity. The influence of the H adsorption site on the hydrogen affinity. The distribution of hydrogen affinity with respect to the termination composition on the both sides of MXenes. The correlations between the hydrogen affinity and the reaction energy of C-H activations.

References
1. F. D. Mango, The Light Hydrocarbons in Petroleum: a Critical Review. *Org. Geochem.*, 1996, 26, 417-440.
2. L. Nykanen and K. Honkala, Selectivity in Propene Dehydrogenation on Pt and Pt$_3$Sn Surfaces from First Principles. *ACS Catal.*, 2013, 3, 3026-3030.
3. K. Sun, A. Chen, M. Liu, H. Zhang, R. Duan, P. Ji, L. Li, Q. Li, C. Li, D. Zhong, K. Mullen and L. Chi, Surface-Assisted Alkane Polymerization: Investigation on Structure-Reactivity Relationship. *J. Am. Chem. Soc.*, 2018, **140**, 4820-4825.

4. Z. Nawaz, Light Alkane Dehydrogenation to Light Olefin Technologies: a Comprehensive Review. *Rev. Chem. Eng.*, 2015, **31**, 413-436.

5. L. Yin and J. Liebscher, Carbon-carbon Coupling Reactions Catalyzed by Heterogeneous Palladium Catalysts. *Chem. Rev.*, 2007, **107**, 133-173.

6. D. H. Wang, T. S. Mei and J. Q. Yu, Versatile Pd(ll)-catalyzed C-H Activation/Aryl-aryl Coupling of Benzonic and Phenyl Acetic Acids. *J. Am. Chem. Soc.*, 2008, **130**, 17676-17677.

7. Q. Sun, C. Zhang, H. Kong, Q. Tan and W. Xu, On-surface Aryl-aryl Coupling via Selective C-H Activation. *Chem. Comm.*, 2014, **50**, 11825-11828.

8. I. M. Ciobica, F. Frechard, R. A. van Santen, A. W. Kleyen and J. Hafner, A DFT Study of Transition States for C-H Activation on the Ru(0001) Surface. *J. Phys. Chem. B*, 2000, **104**, 3364-3369.

9. M. S. Liao, C. T. Au and C. F. Ng, Methane Dissociation on Ni, Pd, Pt and Cu Metal(111) Surfaces - A Theoretical Comparative Study. *Chem. Phys. Lett.*, 1997, **272**, 445-452.

10. M. A. Petersen, S. J. Jenkins and D. A. King, Theory of Methane Dehydrogenation on Pt(110)(1 x 2). Part I: Chemisorption of CHx (x=0–3). *J. Phys. Chem. B*, 2004, **108**, 5909-5919.

11. D. Zhong, J. H. Franke, S. K. Podiyananchari, T. Blomker, H. Zhang, G. Kehr, G. Erker, H. Fuchs and L. Chi, Linear Alkane Polymerization on a Gold Surface. *Science*, 2011, **334**, 213-216.

12. M. L. Yang, Y. A. Zhu, X. G. Zhou, Z. J. Sui and D. Chen, First-Principles Calculations of Propane Dehydrogenation over PtSn Catalysts. *ACS Catal.*, 2012, **2**, 1247-1258.

13. O. A. Barias, A. Holmen and E. A. Blekkan, Propane Dehydrogenation over Supported Pt and Pt-Sn Catalysts: Catalyst Preparation, Characterization, and Activity Measurements. *J. Catal.*, 1996, **158**, 1-12.

14. A. Valcarcel, J. M. Ricart, A. Clotet, F. Illas, A. Markovits and C. Minot, Theoretical Study of Dehydrogenation and Isomerisation Reactions of Propylene on Pt(111). *J. Catal.*, 2006, **241**, 115-122.

15. H. B. Zhu, D. H. Anjum, Q. X. Wang, E. Abou-Hamad, L. Emsley, H. L. Dong, P. Laveille, L. D. Li, A. K. Samal and J. M. Basset, Sn Surface-enriched Pt-Sn Bimetallic Nanoparticles as a Selective and Stable Catalyst for Propane Dehydrogenation. *J. Catal.*, 2014, **320**, 52-62.

16. S. Vajda, M. J. Pellin, J. P. Greeley, C. L. Marshall, L. A. Curtiss, G. A. Ballentine, J. W. Elam, S. Catillon-Mucherie, P. C. Redfern, F. Mehmood and P. Zapol, Subnanometre Platinum Clusters as Highly Active and Selective Catalysts for the Oxidative Dehydrogenation of Propane. *Nat. Mater.*, 2009, **8**, 213-216.

17. F. Besenbacher, I. I. Chorkendorff, B. S. Clausen, B. Hammer, A. M. Molenbroek, J. K. Norskov and I. I. Stensgaard, Design of a Surface Alloy Catalyst for Steam Reforming. *Science*, 1998, **279**, 1913-1915.

18. L. Z. Gai, C. T. To and K. S. Chan, Direct Arylation of Aromatic C-H bond Catalyzed by Phthalocyanine. *Tetrahedron Lett.*, 2014, **55**, 6373-6376.

19. M. Nagarib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi and M. W. Barsoum, Two-dimensional Nanocrystals Produced by Exfoliation of Ti3AlC2. *Adv. Mater.*, 2011, **23**, 4248-4253.

20. Y. Zhou, K. Luo, X. Zha, Z. Liu, X. Bai, Q. Huang, Z. Guo, C.-T. Lin and S. Du, Electronic and Transport Properties of Ti3CO2 MXene Nanoribbons. *J. Phys. Chem. C*, 2016, **120**, 17143-17152.

21. Z. Li and Y. Wu, 2D Early Transition Metal Carbides (MXenes) for Catalysis. *Small*, 2019, **15074736**.

22. M. W. Barsoum, The M_{N+1}AX_N Phases: a New Class of Solids: Thermodynamically Stable Nanolaminates. *Prog. Solid State Ch.*, 2000, **28**, 201-281.

23. Z. Guo, J. Zhou, L. Zhu and Z. Sun, MXene: a promising photocatalyst for water splitting. *Mater. Chem A*, 2016, **4**, 11446-11452.
24. Q. Peng, J. Zhou, J. Chen, T. Zhang and Z. Sun, Cu single atoms on Ti$_2$CO$_3$ as a highly efficient oxygen reduction catalyst in a proton exchange membrane fuel cell. J Mater Chem A, 2019, 7, 26062-26070.

25. Z. W. Seh, K. D. Fredrickson, B. Anasori, J. Kibsgaard, A. L. Strickler, M. R. Lukatskaya, Y. Gogotsi, T. F. Jaramillo and A. Vojvodic, Two-Dimensional Molybdenum Carbide (MXene) as an Efficient Electrocatalyst for Hydrogen Evolution. ACS Energy Lett., 2016, 1, 589-594.

26. G. Gao, A. P. O’Mullane and A. Du, 2D MXenes: A New Family of Promising Catalysts for the Hydrogen Evolution Reaction. ACS Catal., 2016, 7, 494-500.

27. Y. Wen, T. E. Rufford, X. Chen, N. Li, M. Lyu, L. Dai and L. Wang, Nitrogen-doped Ti$_3$C$_2$Tx MXene Electrodes for High-performance Supercapacitors. Nano Energy, 2017, 38, 368-376.

28. W. H. K. Ng, E. S. Gnanakumar, E. Batyrev, S. K. Sharma, P. K. Pujari, H. F. Greer, W. Zhou, R. Sakidja, G. Rothenberg, M. W. Barsoum and N. R. Shiju, The Ti$_3$AlC$_2$ MAX Phase as an Efficient Catalyst for Oxidative Dehydrogenation of n-Butane. Angew. Chem. Int. Ed., 2018, 57, 1485-1490.

29. J. Diao, M. Hu, Z. Lian, Z. Li, H. Zhang, F. Huang, B. Li, X. Wang, D. S. Su and H. Liu, Ti$_3$C$_2$T$_x$ MXene Catalyzed Ethylbenzene Dehydrogenation: Active Sites and Mechanism Exploration from both Experimental and Theoretical Aspects. ACS Catal., 2018, 8, 10051-10057.

30. G. Kumar, S. L. J. Lau, M. D. Krcha and M. J. Janik, Correlation of Methane Activation and Oxide Catalyst Reducibility and Its Implications for Oxidative Coupling. ACS Catal., 2016, 6, 1812-1821.

31. Z. J. Zhao, A. Kulkarni, L. Vilella, J. K. Norskov and F. Studt, Theoretical Insights into the Selective Oxidation of Methane to Methanol in Copper-Exchanged Mordenite. ACS Catal., 2016, 6, 3760-3766.

32. A. A. Latimer, H. Aljama, A. Kakkekhi, J. S. Yoo, A. Kulkarni, C. Tsai, M. Garcia-Melchor, F. Abild-Pedersen and J. K. Norskov, Mechanistic Insights into Heterogeneous Methane Activation. Phys. Chem. Chem. Phys., 2017, 19, 3575-3581.

33. T. Bligaard, J. K. Nørskov, S. Dahl, J. Matthiesen, C. H. Christensen and J. Sehested, The Brønsted–Evans–Polanyi Relation and the Volcano Curve in Heterogeneous Catalysis. J. Catal., 2004, 224, 206-217.

34. J. Cheng, P. Hu, P. Ellis, S. French, G. Kelly and C. M. Lok, Bronsted-Evans-Polanyi Relation of Multistep Reactions and Volcano Curve in Heterogeneous Catalysis. J. Phys. Chem. C, 2008, 112, 1308-1311.

35. A. Vojvodic, F. Calle-Vallejo, W. Guo, S. Wang, A. Toftelund, F. Studt, J. I. Martinez, J. Shen, I. C. Man, J. Rossmeisl, T. Bligaard, J. K. Noorskov and F. Abild-Pedersen, On the Behavior of Bronsted-Evans-Polanyi relations for Transition Metal Oxides. J. Chem. Phys., 2011, 134, 244509.

36. F. Viñes, A. Vojvodic, F. Abild-Pedersen and F. Illas, Brønsted–Evans–Polanyi Relationship for Transition Metal Carbide and Transition Metal Oxide Surfaces. J. Phys. Chem. C, 2013, 117, 4168-4171.

37. J. K. Nørskov, T. Bligaard, A. Logadottir, S. Bahn, L. B. Hansen, M. Bollinger, H. Bengaard, B. Hammer, Z. Sljivancanin, M. Mavrikakis, Y. Xu, S. Dahl and C. J. H. Jacobsen, Universality in Heterogeneous Catalysis. J. Catal., 2002, 209, 275-278.

38. P. Kostestkyy, J. Yu, R. J. Gorte and G. Mpourmpakis, Structure–activity relationships on metal-oxides: alcohol dehydration, Catal. Sci. Technol., 2014, 4, 3861-3869.

39. P. Deshlahra and E. Iglesia, Methanol Oxidative Dehydrogenation on Oxide Catalysts: Molecular and Dissociative Routes and Hydrogen Addition Energies as Descriptors of Reactivity, J. Phys. Chem. C, 2014, 118, 26115-26129.

40. M. Dixit, P. Kostetskyy and G. Mpourmpakis, Structure–Activity Relationships in Alkane Dehydrogenation on γ-Al2O3: Site-Dependent Reactions, ACS Catal., 2018, 8, 11570-11578.

41. A. A. Latimer, A. R. Kulkarni, H. Aljama, J. H. Montoya, J. S. Yoo, C. Tsai, F. Abild-Pedersen, F. Studt and J. K. Norskov, Understanding Trends in C-H bond Activation in Heterogeneous Catalysis. Nat. Mater., 2017, 16, 225-229.
42. A. D. Handoko, K. H. Khoo, T. L. Tan, H. M. Jin and Z. W. Seh, Establishing new scaling relations on two-dimensional MXenes for CO\textsubscript{2} electroreduction, J. Mater. Chem. A, 2018, 6, 21885-21890.

43. A. Hjorth Larsen, J. Jorgen Mortensen, J. Blomqvist, I. E. Castelli, R. Christensen, M. Dulak, J. Friis, M. N. Groves, B. Hammer, C. Hargus, E. D. Hermes, P. C. Jennings, P. Bjerre Jensen, J. Kermode, J. R. Kitchin, E. Leonhard Kolsbjerg, J. Kubal, K. Kaasbjerg, S. Lysgaard, J. Bergmann Maronsson, T. Maxson, T. Olsen, L. Pastewka, A. Peterson, C. Rostgaard, J. Schiotz, O. Schutt, M. Strange, K. S. Thygesen, T. Vegge, L. Vilhelmsen, M. Walter, Z. Zeng and K. W. Jacobsen, The Atomic Simulation Environment - a Python Library for Working with Atoms. J. Phys-Condens Mat., 2017, 29, 273002.

44. G. Kresse and J. Furthmuller, Efficient Iterative Schemes for ab-initio Total-energy Calculations Using a Plane-wave Basis Set. Phys. Rev. B, 1996, 54, 11169-11186.

45. Blöch, Projector Agumented-wave Method. Phys. Rev. B, 1994, 50, 17953.

46. M. Dion, H. Rydberg, E. Schroder, D. C. Langreth and B. I. Lundqvist, Van der Waals Density Functional for General Geometries. Phys. Rev. Lett., 2004, 92, 246401.

47. I. Hamada, Van der Waals Density Functional Made Accurate. Phys. Rev. B, 2014, 89, 121103.

48. G. Henkelman and H. Improved Tangent Estimate in the Nudged Elastic Band Method for Finding Minimum Energy Paths and Saddle Points. J. Chem. Phys., 2000, 113, 9978-9985.

49. G. Henkelman, B. P. Uberuaga and H. Jonsson, A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths. J. Chem. Phys., 2000, 113, 9901-9904.

50. G. Henkelman and H. Jonsson, A Dimer Method for Finding Saddle Points on High Dimensional Potential Surfaces using Only First Derivatives. Special Points for Brillouin-Zone Integrations. J. Chem. Phys., 1999, 111, 7010-7022.

51. H. J. Monkhorst and J. D. Pack, Special Points for Brillouin-Zone Integrations. Phys. Rev. B, 1976, 13, 5188-5192.

52. I. Persson, L. A. Naslund, J. Halim, M. W. Barsoum, V. Darakchieva, J. Palisaitis, J. Rosen and P. O. A. Persson, On the Organization and Thermal Behavior of Functional Groups on Ti\textsubscript{3}C\textsubscript{2}MXene Surfaces in Vacuum. 2D Mater., 2018, 5.

53. T. Hu, Z. Li, M. Hu, J. Wang, Q. Hu, Q. Li and X. Wang, Chemical Origin of Termination-Functionalized MXenes: Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{2} as a Case Study. J. Phys. Chem. C, 2017, 121, 19254-19261.

54. O. Mashtalir, M. Naguib, B. Dyatkin, Y. Gogotsi and M. W. Barsoum, Kinetics of Aluminum Extraction from Ti\textsubscript{3}AlC\textsubscript{2} in Hydrofluoric Acid. Mater. Chem. Phys., 2013, 139, 147-152.

55. J. Halim, K. M. Cook, M. Naguib, P. Eklund, Y. Gogotsi, J. Rosen and M. W. Barsoum, X-ray photoelectron spectroscopy of select multi-layered transition metal carbides (MXenes), Appl. Surf. Sci., 2016, 362, 406-417.

56. Y. Jiang, T. Sun, X. Xie, W. Jiang, J. Li, B. Tian and C. Su, Oxygen Functionalized Ultrathin Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene for Enhanced Electrocatalytic Hydrogen Evolution. ChemSusChem, 2019, 1368-1373.

57. G. Fu, Z. N. Chen, X. Xu and H. L. Wan, Understanding the Reactivity of the Tetrahedrally Coordinated High-valence d(0) Transition Metal Oxides toward the C-H Bond Activation of Alkanes: A Cluster Model Study. J. Phys. Chem. A, 2008, 112, 717-721.

58. E. C. Tyo, C. R. Yin, M. Di Vece, Q. Qian, G. Kwon, S. Lee, B. Lee, J. E. DeBartolo, S. Seifert, R. E. Winans, R. Si, B. Ricks, S. Goergen, M. Rutter, B. Zugic, M. Oxidative Dehydrogenation of Cyclohexane on Cobalt Oxide (Co\textsubscript{2}O\textsubscript{4}) Nanoparticles: The Effect of Particle Size on Activity and Selectivity. ACS Catal., 2012, 2, 2409-2423.

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