Two-Dimensional Titanium and Molybdenum Carbide MXenes as Electrocatalysts for CO₂ Reduction

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HIGHLIGHTS
Combined experimental and theoretical CO₂RR investigation on MXenes

T₅ group stabilizes *H-coordinated intermediates and breaks scaling relations

Formic acid is the main CO₂RR product on Ti₂CT₅ and Mo₂CT₅ MXenes

Lower degree of –F termination in T₅ group results in smaller overpotential

Handoko et al., iScience 23, 101181
June 26, 2020 © 2020 The Author(s).
https://doi.org/10.1016/j.isci.2020.101181
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SUMMARY

Electrocatalytic CO$_2$ reduction reaction (CO$_2$RR) is an attractive way to produce renewable fuel and chemical feedstock, especially when coupled with efficient CO$_2$ capture and clean energy sources. On the fundamental side, research on improving CO$_2$RR activity still revolves around late transition metal-based catalysts, which are limited by unfavorable scaling relations despite intense investigation. Here, we report a combined experimental and theoretical investigation into electrocatalytic CO$_2$RR on Ti- and Mo-based MXene catalysts. Formic acid is found as the main product on Ti$_2$CTx and Mo$_2$CTx MXenes, with peak Faradaic efficiency of over 56% on Ti$_3$CTx and partial current density of up to –2.5 mA cm$^{-2}$ on Mo$_2$CTx. Furthermore, simulations reveal the critical role of the T$_x$ group: a smaller overpotential is found to occur at lower amounts of –F termination. This work represents an important step toward experimental demonstration of MXenes for more complex electrocatalytic reactions in the future.

INTRODUCTION

Efforts to tackle rising CO$_2$ concentration in the atmosphere have been primarily focused on carbon capture and sequestration, as well as decarbonization of the energy and land use sectors (Walsh et al., 2017). However, an equally pressing issue of depleting fossil energy and chemical raw materials is looming. Electrocatalytic CO$_2$ reduction reaction (CO$_2$RR) presents an attractive pathway to achieve both decarbonization of energy economy and production of renewable fuel/chemical feedstock (De Luna et al., 2019; Seh et al., 2017), especially when coupled with increasingly affordable clean electricity (Obama, 2017).

To realize industrial-scale CO$_2$RR, substantial challenges on both the fundamental (i.e., catalyst activity and selectivity) and system levels (i.e., mass transport, conversion rate, and energy efficiency) need to be addressed (Jouny et al., 2018; De Luna et al., 2019; Handoko et al., 2018c; Higgins et al., 2019). On the fundamental side, there has been some progress in understanding CO$_2$RR in liquid electrolytes, with emphasis on late transition metals, particularly copper, owing to its unusual ability to convert CO$_2$ to multi-carbon products (Hori, 2008; Huang et al., 2017). However, despite intense optimization of these transition metal catalysts (Saberi Safaei et al., 2016; Handoko et al., 2016; Mistry et al., 2016; Li et al., 2017b; Ren et al., 2016), their activity and selectivity seem to be limited. One of the most significant barriers limiting fundamental CO$_2$RR on transition metal catalysts appears to be the linear scaling relations between the binding energies of reaction intermediates (Liu et al., 2017). These unfavorable scaling relations due to similarly bound reaction intermediates (e.g., *COOH, *CO, *CHO, “*” refers to a site on the catalyst surface) limit the CO$_2$RR overpotential that can be achieved on pure transition metal surfaces.

One of the most promising ways to improve CO$_2$RR activity is to explore new catalyst material systems that allow stabilization of intermediates with different scaling relations. MXenes, a family of two-dimensional transition metal carbide/nitride materials with metallic-like conductivity (Anasori et al., 2017), present a viable solution. MXenes have a general formula of M$_{x+1}$+nX$_n$T$_x$, where M represents an early transition metal, X is carbon and/or nitrogen, with n in the range of 1–4 (Anasori and Gogotsi, 2019; Deysher et al., 2020). T$_x$ represents surface termination groups, which can include –O, –F, etc. (Hope et al., 2016). The tunable surface and internal configuration of MXenes, including the possibility of mixed surface terminations, as well as mixed metal atoms in solid solution (Yang et al., 2016) or ordered structure (Anasori et al., 2015; Anasori and Gogotsi, 2019), allow for tailoring of intermediates’ binding configuration and strength (Hart et al., 2019; Anasori et al., 2016; Handoko et al., 2018a; Chen et al., 2019), making it an ideal platform to search for active and selective CO$_2$RR catalysts (Handoko et al., 2019). To date, investigations of MXenes for
electrocatalytic CO$_2$RR have been primarily based on theoretical calculations (Li et al., 2017a; Handoko et al., 2018b; Chen et al., 2019; Zhang et al., 2017b), although some works on photocatalytic CO$_2$RR have indicated that MXenes may enhance charge separation or act as co-catalyst (Cao et al., 2018; Ye et al., 2018).

Here, we investigate the electrocatalytic CO$_2$RR activity on Ti$_2$CT$_x$ and Mo$_2$CT$_x$ MXenes using a combination of experiment and theory. These MXenes were chosen as they have Ti and Mo metal sites with opposing hydrogen binding behavior (Laursen et al., 2012). The CO$_2$RR experiments are carried out in mixtures of acetonitrile, water, and 3-butyl-1-methyl-1H-imidazol-3-ium tetra-fluoroborate (BMIMBF$_4$) electrolyte. Formic acid is found to be the main CO$_2$RR product on these MXenes with Faradaic efficiency of 56.1% at $-1.8$ V (all potentials in this work are expressed with respect to the standard hydrogen electrode, SHE). H$_2$ is the main side product, alongside trace amounts of CO, CH$_4$, and other hydrocarbons. More importantly, we demonstrate that the nature of surface terminating group appears to control the CO$_2$RR activity. Specifically, the presence of –F termination group, commonly adsorbed onto MXene surface during synthesis (Hope et al., 2016), was found to alter the binding strength of intermediates and the corresponding CO$_2$RR limiting potential compared to fully –O terminated MXenes, as supported by density functional theory (DFT). Overall, this work provides insights on MXene electrocatalysts that circumvent traditional scaling relations in CO$_2$RR, which can potentially be extended to other promising reactions of interest.

RESULTS

We first investigate the effect of surface termination group T$_x$ on the CO$_2$RR activity of Ti$_2$CT$_x$ MXenes. To achieve this, we synthesized two variants of Ti$_2$CT$_x$ with different surface termination compositions using different etching procedures, namely, 18 h in 10% HF and 48 h in 4 M KF-HCl mixture (refer to the Transparent Methods in the Supplemental Information). These MXenes will be referred to as Ti$_2$CT$_x$ (HF) and Ti$_2$CT$_x$ (KF-HCl), respectively. Previous works suggest that the use of fluoride salt etching solution in place of HF can reduce the amounts of –F terminations (Hope et al., 2016; Handoko et al., 2018a). The scanning electron micrographs of both Ti$_2$CT$_x$ (HF) and Ti$_2$CT$_x$ (KF-HCl) show layered structures after the etching procedure (Figures 1A and 1B), consistent with previously reported morphologies (Anasori et al., 2017). X-ray diffraction (XRD) shows that most of the Ti$_2$AlC precursors are successfully converted to Ti$_2$CT$_x$ with the appearance of the characteristic (002) broad peaks of MXenes around 2$\theta$ = 11.1° and 9.2° for HF and KF-HCl etched Ti$_2$CT$_x$, respectively (Figure 1D; see Figure S1 and Table S1 for characterization of precursors). These peaks correspond to MXene interlayer distances of around 8.0 and 9.6 Å, consistent with previous reports on smaller interlayer distance for HF-etched samples Naguib et al., 2012.

X-ray photoelectron spectroscopy (XPS) of the as-synthesized Ti$_2$CT$_x$ samples in the Ti 2p range detects a mix of Ti species, including Ti-T/C, Ti(III), and more oxidized Ti(IV) species (Figures 2A and 2B; see Tables...
Some degree of Ti(IV) formation is unavoidable in Ti$_2$CT$_x$ as it is less stable against oxidation compared with other MXenes with higher $n$ such as Ti$_3$C$_2$T$_x$ (Zhang et al., 2017a). A comparison of the $F$ to Ti atomic ratio (Tables S3 and S4) shows that Ti$_2$CT$_x$ (HF) has significantly more $-$F surface terminations ($F$/Ti = 0.36) than Ti$_2$CT$_x$ (KF-HCl) ($F$/Ti = 0.21). We have previously shown that the electrocatalytic activities of MXenes are very sensitive to the surface termination (Handoko et al., 2018a), thus we posit that the variation in $-$F termination content on Ti$_2$CT$_x$ samples will alter their CO$_2$RR activity.

As an initial CO$_2$RR activity assessment, we first compared the linear scanning voltammetry (LSV) profile of Ti$_2$CT$_x$ (HF) and Ti$_2$CT$_x$ (KF-HCl) in the presence and absence of CO$_2$ in a mixture of 80:15:5 mol fraction of acetonitrile:water:BMIMBF$_4$ electrolyte (Figure S2). The electrolyte mixture is used in this study owing to prevalent HER in aqueous electrolyte systems like 0.1 M KHCO$_3$ (Figure S3). Dipolar aprotic solvents like acetonitrile have enhanced CO$_2$ solubility compared with aqueous systems (Gennaro et al., 1990). Furthermore, imidazolium-based ionic liquid has been shown to enhance CO$_2$RR (Asadi et al., 2016), possibly by forming complexes with CO$_2$ molecules at moderately cathodic potentials ($\leq 0.1$ V versus SHE) (Matsubara et al., 2015; Rosen et al., 2011).

Under N$_2$ purging, both Ti$_2$CT$_x$ samples display sharp onset potential at around $-1.8$ V (Figures S2A and S2B), which can be attributed to the hydrogen evolution reaction (HER). The introduction of CO$_2$ into the reaction environment changes the LSV profile for both Ti$_2$CT$_x$ samples significantly. Most notably, some cathodic features are observed around $-1.4$ to $-1.8$ V. These features were especially clear on Ti$_2$CT$_x$ (KF-HCl), indicating more significant CO$_2$ (or related intermediates) adsorption and interaction (Salehi-Khojin et al., 2013) compared with Ti$_2$CT$_x$ (HF). Additionally, the HER onset potentials on both Ti$_2$CT$_x$ samples are delayed by about $0.1$ to $-0.2$ V with reduced current density. As the electrolyte pH ($\approx 1.24$) and reference electrode are unaffected by CO$_2$ purging (Figure S4), this HER “poisoning” effect can be attributed to CO$_2$ (or related intermediates) adsorption that competes with H. Such an effect is expected on transition metal surfaces that show weak H binding strength like Ti (Huang et al., 2017; Zhang et al., 2014).

To quantify their CO$_2$RR activity, both Ti$_2$CT$_x$ samples are subjected to chronoamperometric (constant voltage) measurement for 100 min under continuous CO$_2$ gas purging in a two-compartment cell.
Both Ti$_2$CT$_x$ samples retain most of their characteristic XPS peaks after CO$_2$RR, with slight increase in the more oxidized Ti(IV) signals due to ambient exposure during testing (Figures 2D and 2E). Online gas chromatography (GC) and nuclear magnetic resonance (NMR) were used to quantify gaseous and liquid products from CO$_2$RR, revealing formic acid and H$_2$ to be the main products on both Ti$_2$CT$_x$ samples (Figures 3 and S6). It is clear from the Faradaic efficiency (FE) plot (Figure 3A) and partial current density (j) plot (Figure 3B) that Ti$_2$CT$_x$ (KF-HCl) shows enhanced selectivity and turnover for CO$_2$RR to formic acid compared with Ti$_2$CT$_x$ (HF), although the CO$_2$RR onset potentials are similar for both samples at $-1.5$ V. At a potential of $-1.8$ V, Ti$_2$CT$_x$ (KF-HCl) displays 56.1% FE$_{HCOOH}$ compared with 20.7% on Ti$_2$CT$_x$ (HF), with a corresponding 2.5 times higher $j_{HCOOH}$ normalized to geometric surface area. Plots of $j_{HCOOH}$ normalized to electrochemical surface area are also shown in Figure S7 and Table S6.

To gain insight on the experimental results, we turn to DFT calculations to systematically investigate the effect of varying amounts of –F termination group on the theoretical CO$_2$RR overpotential on Ti$_2$CT$_x$ samples. In particular, three different Ti$_2$CT$_x$ structures were modeled with T$_x$ groups comprising (1) 0.0% –F, 100.0% –O, (2) 33.3% –F, 66.7% –O, and (3) 66.7% –F, 33.3% –O (Figure S8). The T$_x$ compositions were selected based on the range of –F termination previously studied on Ti-based MXenes (Handoko et al., 2018a). On fully –O terminated Ti$_2$CT$_x$ surface, CO$_2$RR to formic acid is completed in four steps, including a CO$_2$ adsorption step, two consecutive proton-coupled electron transfer (PCET) steps, and finally an HCOOH (l) desorption step (Figure 4A). In this case, only the *COOH pathway was considered, as the alternative route through HCOO intermediate was found to be unfavorable (Figure S9), consistent with the literature (Li et al., 2017a). The *CO$_2$ + H$^+$ + e$^-$ $\rightarrow$ *COOH step (PCET-1) is predicted to be potential limiting with a free energy change ($\Delta G_{\text{elec}}$) of $0.85$ eV. Hence, the theoretical CO$_2$RR limiting potential ($U_{\text{LCO}_2} = -\Delta G_{\text{elec}}/e$) can be calculated to be $-0.85$ V.

Gradual –F substitution of the –O T$_x$ group in Ti$_2$CT$_x$ results in significant variation of reaction free energy (Figure 4A). Specifically, the PCET-1 potential limiting step becomes more endergonic (larger $\Delta G_{\text{elec}}$) at a higher fraction of –F substitution. As a result, the $U_{\text{LCO}_2}$ becomes more negative at $-0.89$ and $-1.26$ V for 33.3% and 66.7% –F, respectively, possibly due to increasingly unstable *COOH conformations (Figure S8). As *HCOOH adsorption energy does not change substantially with –F substitution, we observe that the PCET-1 reaction step remains potential limiting throughout. This means that the least negative $U_{\text{LCO}_2}$ can only be achieved on fully –O terminated Ti$_2$CT$_x$. These simulation results explain the higher FE$_{HCOOH}$ and $j_{HCOOH}$ observed on Ti$_2$CT$_x$ (KF-HCl) as it has significantly lower –F surface termination compared with Ti$_2$CT$_x$ (HF).

To study if the effect of –F substitution is common to other MXenes, we expand the investigation to Mo$_2$CT$_x$. In this case, only HF etching is used, as milder KF-HCl etchant is not able to etch Mo$_2$Ga$_2$C precursor. Nonetheless, Mo$_2$CT$_x$ could potentially be a better CO$_2$RR catalyst as it tends to have fewer –F terminations than Ti$_2$CT$_x$ even when a harsher etching condition using 48% HF is used (Halim et al., 2016). The morphology of Mo$_2$CT$_x$ is slightly different than Ti$_2$CT$_x$ with less obvious delamination between the layers (Figure 1C), consistent with previous studies (Halim et al., 2016). XRD analyses also indicate successful etching of most Mo$_2$Ga$_2$C precursor, with a broad peak at 2$\theta = 9.0^\circ$ indicative of a (002) interlayer distance of around 9.8 Å (Figure 1D; see Figure S1 and Table S1 for characterization of precursors). XPS shows a
relatively large Mo-Tx/C component with no signs of Mo(VI) (Figure 2C). The F/Mo atomic ratio is estimated to be 0.03 (Table S5).

Initial LSV assessments under N2 purging show earlier HER onset potential on Mo2CTx around –1.3 V (Figure S2C), which is consistent with its superior HER activity (Handoko et al., 2018a; Seh et al., 2016). However, it is unusual that Mo2CTx also displayed a similar HER poisoning effect under CO2 purging since, unlike Ti, Mo should bind to *H strongly (Laursen et al., 2012). The observation of HER poisoning on both MXenes suggests that the interaction of *CO2 or other intermediates with the Tx groups is possibly more critical than that with the base metal sites.

GC and NMR analysis during chronoamperometric measurements revealed that Mo2CTx starts forming formic acid at much less negative potential (–0.9 V) than both types of Ti2CTx (–1.5 V). This is consistent with the cathodic features observed in LSV under CO2 purging (Figure S2C). Although the maximum FE_HCOOH of Mo2CTx (32.6% at –1.3 V, Figure 3A) is lower compared with Ti2CTx (KF-HCl, 56.1% at –1.8 V), the former shows significantly higher j_HCOOH up to 2.5 mA cm$^{-2}_\text{geo}$ at less negative potentials (Figure 3B), suggesting that it is quite active in reducing CO2 to formic acid. The stability of CO2RR on Mo2CTx is assessed by conducting continuous electrolysis for 500 min. Some fluctuation in FE_HCOOH from 39.9% in the 100th minute to 25.7% in the 500th minute was observed (Figure S10A). We attribute the apparent FE_HCOOH instability to the loss of volatile acetonitrile in the electrolyte during continuous purging rather than catalyst deactivation, as no degradation of j_HCOOH is observed (Figure S10B). Gradual evaporation of acetonitrile would alter the electrolyte composition and increase the water proportion, leading to higher HER turnover that dominates the total current density (Figure S10B). Loss of volatile electrolyte component is a common issue for analytical electrochemical systems that require continuous sampling (Lazouski et al., 2020).

Mo2CTx was found to retain most of its characteristic XPS peaks after CO2RR as well (Figure 2F). The earlier onset and higher turnover for CO2RR to formic acid on Mo2CTx is unexpected owing to its predisposition.

Figure 4. Density Functional Theory Calculations for CO2RR to Formic Acid on Ti2CTx and Mo2CTx MXenes
Calculated free energy diagram at 0 V applied potential for CO2RR to formic acid on (A) Ti2CTx and (B) Mo2CTx MXenes with varying fractions of –F and –O surface terminating groups. Blue, purple, red, brown, and white spheres represent Ti, Mo, O, C, and H atoms, respectively.
HCOOH and the T
HCOOH intermediate is favorable on MXenes owing to the hydrogen-bond interaction between –F, but this time at lower fractions of 11.1%, 22.2%, and 33.3% (Figure S11) owing to fewer –F terminations. Less negative ULCO2 is achieved at stronger *COOH binding energy, up to a point where protonation of T
ifies a minimum at 3.8% –F substitution (Figure S12B), indicating that low amounts of –F T
also possesses the least negative ULCO2 value (Figure S12B) nearly on all cases, except on Mo2CTx with 11.1% –F substitution where the limiting potential is close to the ideal value (−0.02 V, Figure S12B).

The difference between the limiting potentials of CO2RR and HER (ULCO2−ULH2) could then be used to gauge the selectivity of the catalysts toward CO2RR (Hong et al., 2016; Shi et al., 2014). In addition to having the least negative ULCO2 value, we found that –O terminated Mo2CTx also possesses the least negative ULCO2−ULH2 difference of −0.1 V (Figure 5C). Quadratic functions fitting of ULCO2−ULH2 on Mo2CTx identifies a minimum at 3.8% –F substitution (Figure S12B), indicating that low amounts of –F T
presence may be beneficial to CO2RR.

Although the ULCO2−ULH2 values on all variants of Ti2CTx and Mo2CTx are still generally negative across all fractions of –F substitutions, we recognize that the kinetics of both HER and CO2RR can be significantly altered by the reaction environment (König et al., 2019). In addition to the enhanced CO2 solubility in acetonitrile, the formation of BMIM-CO2 complex has been shown to enhance CO2 mass transport and significantly boost CO2RR activity (Rosen et al., 2011). Furthermore, the hydrophobic BMIM cation has been
proposed to populate near the catalyst surface and suppress HER upon application of CO2RR-relevant cathodic potentials (Rosen et al., 2012).

Apart from formic acid, we also detected up to 1.1% FE of CO and trace amounts of CH4 and multi-carbon products (Figures S15–S17). Our finding partially validates the CO2RR route via a $\text{HCOOH}$ intermediate (Li et al., 2017a; Handoko et al., 2018b; Chen et al., 2019), although further optimization of MXene surface terminations (Table S7 and S8 and Figures S18–S22) is necessary to enhance the $\text{HCOOH}$ intermediate stability for the production of more reduced moieties like CH4 and multi-carbon products.

DISCUSSION

In this work, we report a combined experimental and theoretical CO2RR investigation on Ti2CTx and Mo2CTx MXenes. Formic acid is found to be the main CO2RR product with maximum FE exceeding 56% at $-1.8$ V versus SHE on Ti2CTx (KF-HCl). In addition, CO, trace amounts of CH4, and other multi-carbon products are also detected. More importantly, we found that the CO2RR activity appears to be correlated with the fraction of –F and –O surface termination groups (T). Ti2CTx (HF) with large amounts of –F (less –O) shows poorer CO2RR activity and selectivity than Ti2CTx (KF-HCl) with lower –F (more –O). Even higher CO2RR activity, up to $-2.5$ mA cm$^{-2}$, is observed on Mo2CTx catalysts with minimal –F fraction.

DFT simulations indicate that the presence of –F destabilizes $\text{COOH}$ and $\text{H}$, thus causing the limiting potential of both CO2RR and HER to become more negative. An exception is found on Mo2CTx, where small amounts of –F substitution is predicted to balance the individual limiting potentials for PCET-1 and PCET-2 steps and yield the smallest overpotential for CO2RR to formic acid. The CO2RR activity on MXene surfaces could be attributed to unique intermediate-T interaction, which results in stabilization of differently
coordinated *COOH and *HCOOH intermediates. The dissimilar binding coordination leads to deviation in linear scaling relations typically observed on late transition metal-based CO₂RR catalysts like copper.

Although the activity and selectivity toward formic acid can be further improved, this work represents an important step toward experimental demonstration of MXenes for electrocatalytic CO₂RR. The detection of trace amounts of CH₄ and other hydrocarbon products indicate that CO₂RR to more complex moieties on MXenes is possible as well. Work is ongoing to further enhance the activity and selectivity of MXene catalysts through material design strategies including surface engineering (Hart et al., 2019), doping (Yu et al., 2019; Li et al., 2018; Gao et al., 2019), and formation of composite/hybrid structures (Handoko et al., 2019; Chi et al., 2018). In addition, we believe that MXenes could be extended to other technologically important electrocatalytic reactions such as nitrogen reduction or methane oxidation, via surface/composition tailoring and catalytic reaction engineering in the future.

Limitations of the Study
This study investigates Ti- and Mo-based MXenes for CO₂RR to HCOOH and demonstrates different reaction pathways that can break the scaling relations seen in pure transition metal catalysts. However, the prevalent HER activity on MXenes requires the use of non-aqueous electrolyte, which can be challenging for reaction scale up. Gradual loss of volatile component of the non-aqueous electrolyte also causes fluctuation in the HCOOH selectivity. Further optimization of MXene surface terminations is necessary to enhance the intermediate stability for the production of more reduced moieties like CH₄ and multi-carbon products. The DFT computational methods employed here only lend insight from the thermodynamic point of view. The actual experimental result also depends on reaction kinetics that is challenging to probe in complicated systems with multiple intermediates like CO₂RR.

Resource Availability
Lead Contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the Lead Contact, Zhi Wei Seh (sehzw@imre.a-star.edu.sg).

Materials Availability
This study did not generate new unique reagents.

Data and Code Availability
This study did not generate/analyze datasets/code.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2020.101181.

ACKNOWLEDGMENTS
This work was supported by the Singapore National Research Foundation (NRF-NRFF2017-04). The authors thank Yury Gogotsi (Drexel University) for providing precursor materials, as well as Hwee Leng Seng (IMRE) and Teddy Salim (NTU FACTS) for XPS measurements.

AUTHOR CONTRIBUTIONS
A.D.H. and Z.W.S. conceived the idea and wrote the manuscript. A.D.H. and B.A. performed materials synthesis. A.D.H. carried out materials characterization and electrochemical testing. H.C. and Q.Z. performed DFT calculations. All the authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.
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Supplemental Information

Two-Dimensional Titanium and Molybdenum Carbide MXenes as Electrocatalysts for CO₂ Reduction

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Supplemental figures and data

Figure S1: Characterisation of the precursor phases before etching: (a, c) Ti$_2$AlC and (b, d) Mo$_2$Ga$_2$C. The resulting MXene phase is inserted in (c and d) to check for presence of precursor phase. A standard Ti$_2$AlC pattern generated from CIF file from materials project (structure mp-12990) is included in (c). Small amounts of Ti$_2$AlC (▲) and Mo$_2$Ga$_2$C (▽) precursor residues were observed. Related to Figure 1.
Table S1: XPS analysis to quantify precursor residues. Related to Figure 1.

| Element | Ti$_2$CT$_x$ (HF) | Element | Ti$_2$CT$_x$ (KF-HCl) | Element | Mo$_2$CT$_x$ (HF) |
|---------|------------------|---------|-----------------------|---------|------------------|
| Ti      | 50.24%           | Ti      | 40.91%                | Mo      | 69.53%           |
| C       | 8.49%            | C       | 24.11%                | C       | 7.61%            |
| O       | 16.43%           | O       | 18.18%                | O       | 15.69%           |
| F       | 17.81%           | F       | 16.79%                | F       | 2.90%            |
| Al      | 7.03%            | Al      | N. Q.                 | Ga      | 4.28%            |

N.Q.: not quantified due to very low signal to noise ratio.

Table S2: Oxidation state fraction of “M” elements in M$_2$CT$_x$ MXenes. Related to Figure 2.

|         | Ti$_2$CT$_x$ (HF) | Ti$_2$CT$_x$ (KF-HCl) | Mo$_2$CT$_x$ (HF) |
|---------|------------------|-----------------------|-------------------|
|         | pre-CO$_2$RR     | post-CO$_2$RR         | pre-CO$_2$RR      | post-CO$_2$RR |
| M-T$_x$/C (MXene) | 37.7%       | 27.3%                  | 26.8%         | 19.6%        | 49.4%   | 21.5%   |
| Ti(II)  | 55.9%           | 47.6%                  | 46.6%         | 28.0%        | n.a.     | n.a.    |
| Ti(IV)  | 6.4%            | 25.1%                  | 26.6%         | 52.4%        | n.a.     | n.a.    |
| Mo(V)   | n.a.            | n.a.                  | n.a.          | n.a.         | 50.6%    | 48.6%   |
| Mo(VI)  | n.a.            | n.a.                  | n.a.          | n.a.         | n.a.     | 29.9%   |

Table S3: XPS details for Ti$_2$CT$_x$ (HF) before CO$_2$RR. Related to Figure 2.

| Element | Samples | Average | Stdev |
|---------|---------|---------|-------|
| Ti      | 1       | 44.77%  | 2.91% |
|         | 2       | 37.15%  | 39.04%| 39.49%| 50.17%| 43.27%| 5.52% |
|         | 3       | 48.98%  | 39.04%| 39.49%| 50.17%| 43.27%| 5.52% |
|         | 4       | 39.04%  | 39.49%| 50.17%| 43.27%| 5.52% |
|         | 5       | 48.98%  | 39.49%| 50.17%| 43.27%| 5.52% |
|         | 6       | 39.04%  | 39.49%| 50.17%| 43.27%| 5.52% |
| C       | 1       | 10.98%  | 10.65%| 30.81%| 31.00%| 31.55%| 1.30% |
|         | 2       | 14.95%  | 26.56%| 25.15%| 17.13%| 17.84%| 7.22% |
|         | 3       | 26.56%  | 25.15%| 17.13%| 17.84%| 7.22% |
|         | 4       | 14.95%  | 26.56%| 25.15%| 17.13%| 17.84%| 7.22% |
|         | 5       | 30.81%  | 31.00%| 31.55%| 1.30%  |       |
|         | 6       | 31.00%  | 31.55%| 1.30%  |       |
| O       | 1       | 21.24%  | 14.78%| 37.15%| 37.15%| 27.43%| 7.22% |
|         | 2       | 26.24%  | 25.58%| 37.15%| 37.15%| 27.43%| 7.22% |
|         | 3       | 37.15%  | 37.15%| 27.43%| 27.43%| 7.22% |
|         | 4       | 25.58%  | 37.15%| 27.43%| 27.43%| 7.22% |
|         | 5       | 37.15%  | 37.15%| 27.43%| 27.43%| 7.22% |
|         | 6       | 37.15%  | 37.15%| 27.43%| 27.43%| 7.22% |
| F       | 1       | 23.01%  | 10.66%| 10.66%| 10.66%| 10.66%| 4.94% |
|         | 2       | 20.16%  | 10.66%| 10.66%| 10.66%| 10.66%| 4.94% |
|         | 3       | 10.66%  | 10.66%| 10.66%| 10.66%| 4.94% |
|         | 4       | 10.66%  | 10.66%| 10.66%| 10.66%| 4.94% |
|         | 5       | 10.66%  | 10.66%| 10.66%| 10.66%| 4.94% |
|         | 6       | 10.66%  | 10.66%| 10.66%| 10.66%| 4.94% |

Average F/Ti = 0.36

Table S4: XPS details for Ti$_2$CT$_x$ (KF-HCl) before CO$_2$RR. Related to Figure 2.

| Element | Samples | Average | Stdev |
|---------|---------|---------|-------|
| Ti      | 1       | 36.00%  | 2.91% |
|         | 2       | 35.04%  | 33.22%| 28.70%| 31.51%| 32.89%| 2.91% |
|         | 3       | 33.22%  | 28.70%| 31.51%| 32.89%| 2.91% |
|         | 4       | 28.70%  | 31.51%| 32.89%| 2.91% |
|         | 5       | 31.51%  | 32.89%| 2.91% |
| C       | 1       | 26.97%  | 33.22%| 28.70%| 31.51%| 32.89%| 2.91% |
|         | 2       | 26.86%  | 33.22%| 28.70%| 31.51%| 32.89%| 2.91% |
|         | 3       | 26.56%  | 33.22%| 28.70%| 31.51%| 32.89%| 2.91% |
|         | 4       | 26.56%  | 33.22%| 28.70%| 31.51%| 32.89%| 2.91% |
|         | 5       | 26.56%  | 33.22%| 28.70%| 31.51%| 32.89%| 2.91% |
| O       | 1       | 30.97%  | 33.22%| 28.70%| 31.51%| 32.89%| 2.91% |
|         | 2       | 31.09%  | 33.22%| 28.70%| 31.51%| 32.89%| 2.91% |
|         | 3       | 33.22%  | 28.70%| 31.51%| 32.89%| 2.91% |
|         | 4       | 33.22%  | 28.70%| 31.51%| 32.89%| 2.91% |
|         | 5       | 33.22%  | 28.70%| 31.51%| 32.89%| 2.91% |
| F       | 1       | 6.07%   | 7.21% | 6.34% | 7.09% | 8.09% | 6.96% |
|         | 2       | 7.21%   | 6.34% | 7.09% | 8.09% | 6.96% | 0.80% |
|         | 3       | 6.34%   | 7.09% | 8.09% | 6.96% | 0.80% |
|         | 4       | 7.09%   | 8.09% | 6.96% | 0.80% |
|         | 5       | 8.09%   | 6.96% | 0.80% |

Average F/Ti = 0.21
Table S5: XPS details for Mo$_2$CT$_x$ (HF) before CO$_2$RR. Related to Figure 2.

| Element | Samples | Average | Stdev |
|---------|---------|---------|-------|
|         | 1       | 2       | 3     | 4     | 5       |
| Mo      | 54.82%  | 72.64%  | 64.47%| 65.76%| 66.98%  | 64.93%  | 6.45%   |
| C       | 12.69%  | 7.95%   | 9.61% | 5.71% | 6.11%   | 8.41%   | 2.85%   |
| O       | 29.83%  | 16.39%  | 24.11%| 27.08%| 25.71%  | 24.63%  | 5.06%   |
| F       | 2.65%   | 3.03%   | 1.81% | 1.44% | 1.20%   | 2.03%   | 0.79%   |

Average F/Mo = 0.03
Figure S2: Linear scanning voltammetry (LSV) scans of MXenes in the presence and absence of CO\textsubscript{2}: (a) Ti\textsubscript{2}CT\textsubscript{x} (HF), (b) Ti\textsubscript{2}CT\textsubscript{x} (KF-HCl), and (c) Mo\textsubscript{2}CT\textsubscript{x} (HF). Electrolyte: acetonitrile-\textsubscript{H}\textsubscript{2}O-BMIMBF\textsubscript{4} mixture. Gas purging: N\textsubscript{2} and CO\textsubscript{2} purged as marked. iR drop is compensated via positive feedback correction at 85% of estimated R\textsubscript{u} obtained by electrochemical impedance spectroscopy (EIS) measurement. Related to Figure 3.
Figure S3: CO$_2$RR on Ti$_2$CT$_x$ (KF-HCl) in 0.1 M KHCO$_3$ aqueous electrolyte. All conditions identical except that the electrolyte in both anodic and cathodic compartments is replaced with CO$_2$ purged 0.1 M KHCO$_3$ aqueous solution. Related to Figure 3.
Figure S4: Cyclic voltammetry (CV) of glassy carbon electrode in acetonitrile-H$_2$O-BMIMBF$_4$ electrolyte with 5 mM of ferrocene. (b) Comparison of N$_2$ and CO$_2$ purged electrolyte. The reference electrode used in this work is calibrated by conducting CV scans in acetonitrile-H$_2$O-BMIMBF$_4$ electrolyte mixture in the presence of 5 mM ferrocene. Average of anodic going and cathodic going first derivative of the CV cycle is determined to be 0.21 V. Fc/Fc$^{+}$ redox potential in acetonitrile solution is taken at 0.624 V vs. SHE, (Pavlishchuk and Addison, 2000) thus the conversion value of Ag/AgCl in acetonitrile-H$_2$O-BMIMBF$_4$ electrolyte mixture is determined to be 0.414 V. We further determine that the Fc/Fc$^{+}$ reaction and reference electrode is unchanged in presence of CO$_2$ purging, indicating that the bicarbonate buffer system is insignificant in our electrolyte system. Related to Figure 3.
Figure S5: Schematic of two-compartment electrochemical cell used for CO$_2$RR in this work. Related to Figure 3.
Figure S6: FE of CO₂RR major products for (a) Ti₂CTₓ (HF); (b) Ti₂CTₓ (KF-HCl); and (c) Mo₂CTₓ (HF). Related to Figure 3.
Figure S7: Plot of geometric current density in consecutive CV measurements at varying scan speeds to estimate double layer capacitance in (a) Ti$_2$CT$_x$ (HF), (b) Ti$_2$CT$_x$ (KF-HCl), and (c) Mo$_2$CT$_x$ (HF). (d) Relative electrochemical surface area (ECSA) normalised partial current density of CO$_2$RR to formic acid on Ti$_2$CT$_x$ and Mo$_2$CT$_x$ MXenes. Error bars represent one standard deviation of three independent measurements. Related to Figure 3.

Table S6: Tabulation of measured double layer capacitance value and the respective normalised surface area of MXenes. Related to Figure 3.

|                  | Ti$_2$CT$_x$ (HF) | Ti$_2$CT$_x$ (KF-HCl) | Mo$_2$CT$_x$ (HF) |
|------------------|-------------------|-----------------------|-------------------|
| Capacitance value (μF) | 29.2              | 59.5                  | 192.8             |
| Normalised       | 1                 | 2.03                  | 6.59              |
Figure S8: Top and side view of *COOH intermediate conformation on Ti$_2$CT$_x$ surface with different Ti groups: (a-b) fully –O terminated, (c-d) 33.3% –F 66.7% –O terminated, (e-f) 66.7% –F 33.3% –O terminated, (g-h) fully –F terminated. Related to Figure 4.
Figure S9: Calculated free energy diagram at 0 V applied potential for CO₂RR to formic acid through an alternative HCOO pathway compared to the *COOH pathway on Ti₂CTₓ (33.3% –F, 66.7% –O). Related to Figure 4.
Figure S10: (a) Periodic sampling of HCOOH concentration during 500 mins CO$_2$RR on Mo$_2$CT$_2$ showing the Faradaic efficiency (squares, left axis) and the measured HCOOH concentration (orange bars, right axis), as well as (b) total current density and HCOOH partial current density. The apparent Faradaic efficiency instability is attributed to change in electrolyte composition due to loss of acetonitrile, resulting in a significant increase in hydrogen evolution activity while maintaining CO$_2$RR to HCOOH. This is reflected in the increased total current density and relatively stable HCOOH partial current density. Related to Figure 3.
Figure S11: Top and side view of *COOH intermediate conformation on Mo$_2$CT$_x$ surface with different T$_x$ groups: (a-b) fully –O terminated, (c-d) 11.1% –F 88.9% –O terminated, (e-f) 22.2% –F 77.8% –O terminated, and (g-h) 33.3% –F 66.7% –O terminated. Related to Figure 4.
Figure S12: Fitting function diagram of the (a) *COOH and *H free energy and (b) the corresponding limiting potentials for CO₂RR, HER and the difference between the two (UL_{CO₂}-UL_{H₂}) on Mo₂CTₓ MXene at varying –F Tₓ fraction. Related to Figure 5.
Figure S13: Charge deformation density of adsorbed *HCOOH intermediates on Ti$_2$CT, (a) fully –O terminated, (b) 33.3% –F 66.7% –O terminated, (c) 66.7% –F 33.3% –O terminated, and Mo$_2$CT, (d) fully –O terminated, (e) 11.1% –F 88.9% –O terminated, (f) 22.2% –F 77.8% –O terminated, and (g) 33.3% –F 66.7% –O terminated. Iso-surfaces drawn represent 0.002 e bohr$^3$. Charges flow out from blue areas to yellow areas. Related to Figure 5.
Figure S14: Calculated free energy diagram of HER at 0 V applied potential on (a) Ti$_2$CT$_x$ and (b) Mo$_2$CT$_x$ at varying −F/T$_x$ fraction. Related to Figure 5.
Figure S15: (a) FE data for minor product (CO) and (b) representative gas chromatogram FID of Ti$_2$CT$_x$ and Mo$_2$CT$_x$ at -1.5 V showing trace levels of CO and CH$_4$. Other products C$_2$H$_4$, C$_2$H$_6$ and C$_3$H$_8$ are not quantified due to low amounts. Related to Figure 3.
Figure S16: GC calibration plot for (a) H\textsubscript{2} (b) CO (c) CH\textsubscript{4} (d) C\textsubscript{2}H\textsubscript{4} (e) C\textsubscript{2}H\textsubscript{6} (f) C\textsubscript{3}H\textsubscript{6} and (g) C\textsubscript{3}H\textsubscript{8}. Calibrations were performed at 20 sccm flowrate. The balance gas for all calibration gases is CO\textsubscript{2}.

Related to Figure 3.
Figure S17: NMR calibration plot for formic acid. Mixtures of different concentrations of formic acid are prepared in the same composition of acetonitrile-H$_2$O-BMIMBF$_4$ mixture as the electrolyte used in this study. Integrated NMR area ratio is calculated with respect to the internal standard (50 mM tetramethyl silane in acetonitrile) area. Related to Figure 3.
Table S7: Surface energy of different types of Ti$_2$CT$_x$. The most favourable T$_x$ surface termination sites (fcc or hcp) with lowest surface energy are marked in red. Related to Figure 4.

|       | Surface energy (eV) |
|-------|---------------------|
|       | -F Substitution     | 0.0%    | 33.3%  | 66.7%  | 100.0% |
| fcc   |                     | -405.35 | -390.44| -374.67| -357.66|
| hcp   |                     | -388.96 | -377.74| -366.44| -352.73|

Table S8: Surface energy of different types of Mo$_2$CT$_x$. The most favourable T$_x$ surface termination sites (fcc or hcp) with lowest surface energy are marked in red. Related to Figure 4.

|       | Surface energy (eV) |
|-------|---------------------|
|       | -F Substitution     | 0.0%    | 11.1%  | 22.2%  | 33.3%  | 66.7%  | 100.0% |
| fcc   |                     | -405.21 | -402.96| -398.20| -394.17| -377.34| -358.09|
| hcp   |                     | -414.71 | -409.59| -403.96| -397.10| -375.26| -355.50|
Figure S18: –F termination distribution pattern for 33.3% -F substituted Ti$_2$CT. The calculated energies are (a) -389.88 eV, (b) -389.95 eV, (c) -390.03 eV, and (d) -390.44 eV. Related to Figure 4.

Figure S19: –F termination distribution pattern for 66.7% –F Ti$_2$CT. The calculated energies are (a) -374.11 eV, (b) -374.21 eV, (c) -374.31 eV, (d) -374.67 eV. Related to Figure 4.
Figure S20: –F termination distribution pattern for 22.2% –F Mo₂CTₓ. The calculated energies are (a) -403.66 eV, (b) -403.96 eV. Related to Figure 4.

Figure S21: –F termination distribution pattern for 33.3% –F Mo₂CTₓ. The calculated energies are (a) -396.26 eV (b) -396.32 eV (c) -396.46 eV (d) -397.10 eV. Related to Figure 4.
Figure S22: –F termination distribution pattern for 66.7% –F Mo₂CT₆. The calculated energies are (a) -377.15 eV, (b) -376.65 eV, (d) -376.26 eV, (d) -377.34 eV. Related to Figure 4.
Transparent Methods

Synthesis

Ti₂AlC was synthesised following previously reported procedure (Handoko et al., 2018). Typically, TiC, Ti, and Al powders (Alfa Aesar) with average particle sizes of 2 µm, <44 µm and <44 µm, respectively, were ball milled for 24 h using zirconia balls in a plastic jar. The TiC : Ti : Al molar ratio was 0.85 : 1.15 : 1.05. The powder mixture was heated in an alumina crucible at 5 °C min⁻¹ to 1400 °C and held for 4 h under flowing Ar. After furnace cooling, the porous compact was milled using a TiN-coated milling bit and sieved through a 400 mesh sieve to make Ti₂AlC powder with particle size <37 µm.

Mo₂Ga₂C synthesis methods were described previously (Hu et al., 2015). In brief, 2:1 molar ratio of Mo and C powders (Alfa Aesar) were first heated at 1000 °C for 12 h in Ar environment. The resulting Mo₂C solid was crushed into a powder and homogeneously mixed with melted Ga (at 45 °C) in mortar and pestle with 1:8 molar ratio. The solidified mixture was then vacuum sealed inside quartz tube. The quartz tube then heated at a rate of 10 °C min⁻¹ to 850 °C, and held at that temperature for 48 h. The resulting powder was immersed in a 37 wt% HCl after cooling for 3 days to dissolve possible residual Ga or Ga₂O₃. The final Mo₂Ga₂C powders were sieved to achieve particle size of <37 µm and kept under argon filled glovebox until further use.

HF etched Ti₂CTₓ and Mo₂CTₓ MXenes were prepared as reported previously (Anasori et al., 2017). Typically, 2 g of Ti₂AlC or Mo₂Ga₂C powders were added slowly (over ≈2 min) onto 20 mL of 10 wt% (or 48 wt% for Mo₂Ga₂C) HF solution (Merck) and held for 18 h (or 7 days for Mo₂Ga₂C) at ambient temperature (or 55 °C for Mo₂Ga₂C) inside a Teflon container while stirring at 200 rpm. After that the mixtures were washed at least 5 times by adding deionized (DI) water (18.2 MΩ•cm, Purelab Option Q), shaken for 1 min using a vortex shaker and centrifuging for 5 min at 5000 rpm until a pH of >6. The powders were then dried under vacuum at 50 °C and kept under argon filled glovebox until further use.

To make fluoride salt etched Ti₂CTₓ (Liu et al., 2017), solution containing 4.70 g of KF (99%, Merck) is slowly mixed into 20 mL HCl (36-38%, electronic grade, Duksan Reagents) under magnetic stirring (200 rpm) for 10 minutes inside a Teflon container. Afterwards, 2 g of Ti₂AlC is poured slowly over 2 mins to the solution, and kept under stirring (200 rpm) for 48 h at 40 °C. The samples were then washed with DI water 5 times and ethanol 2 times until pH of supernatant is around 7. The powders were then dried under vacuum at 50 °C and kept under argon filled glovebox until further use.

Characterisation

Morphology of the materials are characterised using JEOL JSM-7600F Schottky Field Emission Scanning Electron Microscope (SEM) operating at 5 kV and 116 µA emission power. Gentle beam
mode is applied at a reduced 1 kV emission voltage to minimise surface charging on non-conductive precursor phases.

Phase composition of the materials was characterised using X-ray diffraction (XRD) using Bruker Advance D8 diffractometer (Cu Kα, λ = 1.541058 Å) fitted with Ni filter and LynxEye XE energy dispersive 1-D detector at 40 kV 40 mA operating power. Coupled 0-2θ scans were performed from 3 to 85° 2θ range with 0.02° step size and 0.3 s time per step. A motorised variable aperture was programmed to provide a fixed 10 mm sample irradiation length to enhance signals at higher 2θ angles. A beam knife is fitted about 1 mm above the sample to minimise air scattering signal at low 2θ angles. Powders were packed into a zero background diffraction plate with ⌀10 mm × 0.2 mm cavity depth (off-cut Si, MTI Corporation) to reduce background contribution.

Elemental analyses is done using X-ray photoelectron spectroscopy (XPS) using a Thermo ThetaProbe or Kratos Axis Supra with a monochromatic Al Kα X-ray source (1486.7 eV). Two consecutive measurements were conducted. The first is to obtain energy calibration signal from adventitious C 1s peak at 284.8 eV. The second measurement was performed after sputtering the sample with Ar⁺ ion gun for ~600 s to remove surface contamination and better identify C 1s, Ti 2p or Mo 3d components belonging to MXene. XPS fitting was done using Avantage software (V6.01, Thermo Scientific), with fitting assignment following the literature (Mashtalir et al., 2013, Halim et al., 2016).

Electrochemical CO₂ reduction

All CO₂RR were performed inside a custom made, two-compartment PTFE electrochemical cell at room temperature (23-25 °C). Each compartment is of 11 mL volume, and separated by 7×2 cm² Nafion 117 membrane (Chemours). The cathodic compartment is filled with 8 mL mixture of acetonitrile (80 mol%, HPLC grade, VWR Chemicals) and DI water (15 mol%, 18.2 MΩ•cm, Purelab Option-Q) as solvent, with 3-butyl-1-methyl-1H-imidazol-3-iium tetra-fluoroborate ionic liquid (5 mol%, BMIMBF₄, 98%, Combi Blocks) added in as supporting electrolyte. The pH of the electrolyte is 1.24. The addition of water is essential as a proton source and to manage the solution viscosity. (Rosen et al., 2013, Yang et al., 2019) The anodic compartment is filled with 8 mL of 0.5 M H₂SO₄ (Merck Ultrapur) as proton reservoir (Lu et al., 2018).

A leakless Ag/AgCl (eDAQ) was used as reference electrode, placed 2 mm above the working electrode. The reference was calibrated with ferrocene and the potential in this work is reported against SHE, by taking the average redox potential of Fc/Fc⁺ to be 0.624 V vs. SHE in acetonitrile solution at 25 °C (Pavlishchuk and Addison, 2000). Electrochemical measurements were done using a calibrated potentiostat (Gamry 600+ or Gamry 3000). Electrolyte resistance was measured each time using high frequency electrochemical impedance spectroscopy and compensated using positive feedback correction at 85% level. The typical Rᵣ Compensation applied is around 8.5-9.5 Ω.
The working electrode substrate is $\varnothing 15 \text{ mm x 1 mm}$ vitreous carbon discs (Goodfellow), polished to mirror finish with 1 $\mu$m alumina slurry followed by 0.3 $\mu$m alumina slurry (Buehler). After each polishing steps, the substrate is ultrasonicated in DI water twice for 5 minutes each. To prepare the catalyst ink, 5 mg of MXene is added into 0.6 mL DI water and 0.4 mL ethanol (absolute grade, VWR Chemicals) and 40 uL of Nafion solution (5% mixture in lower aliphatic alcohol and water, Sigma Aldrich). The ink is then homogenised in an ice bath (approx. 0-4 °C) inside an ultrasonicator for 15 minutes, vortex shaken (2400 rpm) for 1 minute and deposited volumetrically onto the polished glassy carbon to achieve 0.5 mg cm$^{-2}$ loading per vitreous carbon substrate. The catalyst ink is then dried under table lamp (100 W lightbulb). The exposed geometric surface area is 1.327 cm$^2$. Spectroscopically pure graphite rod (Ted Pella) was used as the counter electrode.

CO$_2$ gas (99.999%, Linde Gas) was delivered to both compartments of the electrochemical cell using calibrated mass flow controller (MC 100SCCM-D, Alicat Scientific) at 20 sccm flowrate. The samples were subjected to chronoamperometric (constant voltage) measurement for 100 mins under continuous CO$_2$ gas purging. Periodic sampling every 12.45 minutes was done by an online custom valve gas chromatograph (GC; Wasson-ECE) for gas products quantification. The GC is equipped with a thermal conductivity detector (N$_2$ carrier gas, 99.9995%, Leeden National Oxygen) for detecting H$_2$ and flame ionization detectors (He carrier gas, 99.9995%, Leeden National Oxygen) with a methaniser for detecting C$_1$ to C$_3$ hydrocarbons and CO. Chromatograms were processed using Openlab CDS (Chemstation edition, rev. C.01.08, Agilent Technologies). Gaseous products were calibrated with 6 standard gas mixtures in CO$_2$ balance gas. (AG Gases Ltd., mixtures traceable to standards at the National Physical Laboratory, UK).

Liquid products were analysed using 500 MHz nuclear magnetic resonance (NMR; JEOL JNM-ECA500II), operated with DANTE selective excitation sequence (Morris and Freeman, 1978) (2 $\mu$s pulse, 0.1 ms interval, 40 dB RF output) to suppress high concentration solvent signals. Each spectra is an average of 64-128 consecutive scans. Data was processed using JEOL Delta V5.2. To prepare sample for NMR analysis, 1 mL of sample is mixed with 50 uL of internal standard (50 mM tetramethyl silane in acetonitrile, Cambridge Isotope Lab, 99.9%). 0.5 mL of this mixture is then mixed with 0.1 mL of acetonitrile-D$_3$ (Cambridge Isotope Lab, 99% D). NMR calibration is performed using variable concentrations of formic acid in acetonitrile-H$_2$O-BMIMBF$_4$ electrolyte in the presence of internal standard and acetonitrile-D$_3$. The Faradaic efficiency was calculated by comparing the number of electrons required for the amounts of detected products and the recorded number of electrons measured by the potentiostat (Ren et al., 2015).

**DFT calculation details**

First-principle calculation in the framework of density functional theory (DFT) was applied for all the simulations by using the Vienna ab-initio Simulation Package (VASP) (Kresse and Furthmüller, 1996).
The projector-augmented-wave (PAW) pseudopotential was adopted to treat the core electrons (Blöchl, 1994). Perdew-Burke-Enzerhof (PBE) formulation based on the generalized gradient approximation (GGA) exchange-correlation was utilized to simulate the electron interactions (Perdew et al., 1996). To take Van der Waals force into consideration, correction using DFT-D3 formalism is adopted (Grimme et al., 2010, Grimme et al., 2011). A cut-off energy 450 eV was applied for all computations. Geometry optimization process were fully carried out, and the energy convergence criteria on each atom was 0.03 eV Å\(^{-1}\). The thickness of vacuum is at least 20 Å to avoid artificial interactions amongst the periodic slabs. The 3×3×1 Monkhorst-Pack \(k\)-point mesh sampled Brillouin zone was used for 3×3 supercells.

The computational hydrogen electrode (CHE) was employed, avoiding the explicit treatment of solvated protons (Nørskov et al., 2005). The change of free energy at 0 V (vs. RHE) can be calculated by the following equation:

\[
\Delta G = \Delta E_{elec} + \Delta E_{ZPE} - T \times \Delta S
\]

Where \(\Delta E_{elec}\) is the electronic energy difference between two contiguous reaction steps, \(\Delta E_{ZPE}\) is the difference of the zero-point energy, \(T\) is the temperature and assumed as 298.15 K, while \(\Delta S\) is the difference of the entropy. \(ZPE\) and vibrational entropy of adsorbates are calculated from vibrations by standard methods, which is treated in the harmonic oscillator approximation (Cramer and Bickelhaupt, 2003). As for the gas-phase molecule, the thermal corrections of translations and rotations is also included.

Prior to calculating CO\(_2\)RR intermediates, the most preferred \(T_s\) sites with lowest energy for four Ti\(_2\)CT\(_x\) and five Mo\(_2\)CT\(_x\) models with varying –F substitution levels are first determined. The different distributions of –F atoms at various substitution levels to –OT\(_x\) groups are also taken into consideration. Mo\(_2\)CT\(_x\) models with 66.7% and 100% –F substitution are excluded from further calculations due to significant structure distortion. Ti\(_2\)CT\(_x\) with 100% –F substitution is also excluded due to unstable intermediate adsorption.
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