Unveiling the spontaneous conversion of layered MAX phases to 2D MXenes

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Contributions

T.H. conducted the DFT calculations, built the model, and wrote the manuscript. S.H.Z. and Z.J.L. conducted the etching experiment. C.Z. prepared the MAX phases precursor. X.H.W. supervised the project and edited the manuscript.

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Abstract

Topochemically transforming layered non-van der Waals solid into two dimensional (2D) materials involves selective etching reactions with atomic precision. The element-specific, structure-sensitive
etching at nanoscale urgently requires in-depth understanding. Here, by means of density functional theory calculations and a laboratory-made operando reaction monitoring platform, the mechanism of instantaneous transforming MAX phase into MXenes is unraveled. The overall etching kinetics exhibits a sigmoidal curve, following self-accelerating reaction character with a small activation energy of ca. 60 kJ/mol. Interestingly, this activation energy corresponds to the Al transport through Ti$_3$C$_2$ slits. Therefore the reaction of Al with hydrofluoric acid solution in the confined interlayer space is recognized as the rate-determining step. Last but not the least, we found that the match of A element and etchants to form stable products is critical for the etching reaction, and reaction energy derived from the thermodynamics provides an easy yet effective descriptor for screening efficient etchants.

**Introduction**

Topochemically etching off specific element from covalently bonded layered compounds is a promising strategy for developing novel 2D materials.\(^1\) Such an exfoliation method leads to the synthesis of a series of atomically-thick metastable materials with unique structures and has achieved triumph in two-dimensional transition metal carbides/nitrides (MXenes)\(^2\) and borides (MBene)\(^3\)–\(^5\). This is hardly achieved by conventional method. Topochemical etching method traces its history to the synthesis of silicon nanosheets and other Si-based nanomaterials years ago.\(^6\),\(^7\) Though topochemical etching has enabled many 2D materials from layered non-van der Waals compounds, the mechanism of the etching process is seldom treated. Topochemical conversion of non-van der Waals solids to 2D materials is of increasing significance which requires in-depth understanding.\(^8\) Despite of the importance in 2D material synthesis, the etching with atomic precision is also a promising strategy for atomic and close-to-atomic scale manufacturing.

MXene is one of the most extensively and intensively studied 2D materials after graphene.\(^1\) Holding promise in various applications such as energy storage,\(^9\),\(^10\) energy transformation,\(^11\) and electromagnetic shielding materials,\(^12\) MXenes have been attracting increasing attentions since they were first introduced by topochemical etching strategy.\(^13\) Generally, the MXenes can be produced by selectively etching off the
A elements from MAX phases wherein A element layers are sandwiched by covalent MX layers (M represents early transition metal, A is group III A or IV A element, and X is C and/or N). This process can also be realized by polar organic solvents etching, anodic etching, element replacement by reaction with Lewis acidic molten salts, or hydrothermal etching strategy. Topochemical reaction is so important that it is currently the only effective approach to many novel 2D materials obtained from non-van der Waals solids. Besides, there are more layered non-van der Waals solids have not been exfoliated yet. The limit knowledge of topochemical reaction and inefficient trial-and-error have hindered the development of this method. Moreover, the kinetics for the selective chemical etching process remains unclear, which greatly attracts our interests.

In this work, by means of a combination of DFT calculations and operando experiment, we present an atomistic understanding of the topochemical reaction by taking selectively etching of Ti₃AlC₂ in HF aqueous solution as an example. The main contents are designed as following: First, bonding and energetics of Ti₃AC₂ (A=Al and Si) MAX phases were closely checked. Then thermodynamics of A extraction and MX functionalization, as well as detailed kinetics were evaluated for etching of MAX phases. Next, based on the online monitoring of gas species and volume during etching process, reaction kinetics was worked out. Last but not the least, reaction energy was recognized as an effective descriptor of selective etching. We believe the study would impact on three aspects: (i) elucidating the mechanism of topochemical transition of MAX phases towards MXenes; (ii) atomistic understanding of topochemical reactions; and (iii) guiding the selection of efficient etchants.

Results

Bonding and energetics of Ti₃AC₂ (A=Al and Si) MAX phases. According to previous studies, the Al atom layer sandwiched by Ti₃C₂ layers is able to react with HF solution, generating H₂ molecules and resulting in Ti₃C₂ MXene (equation 1). Ti₃SiC₂ can also be etched by HF solution combined with oxidant
assistantance. For comparison, the hypothetical chemical reaction of HF and Ti₃SiC₂ (equation 2) resembling HF etching Ti₃AlC₂, is also considered here. The bare Ti₃C₂ layers with dangling bonds on the surface can combine HF or H₂O to form functional groups on the surface according to the formulas (3–5).

\[
\begin{align*}
Ti_3AlC_2 + 3HF &= Ti_3C_2 + AlF_3 + 1.5H_2 \\
Ti_3SiC_2 + 4HF &= Ti_3C_2 + SiF_4 + 2H_2 \\
Ti_3C_2 + 2HF &= Ti_3C_2F_2 + H_2 \\
Ti_3C_2 + 2H_2O &= Ti_3C_2(OH)_2 + H_2 \\
Ti_3C_2 + 2H_2O &= Ti_3C_2O_2 + 2H_2
\end{align*}
\]

The extraction of A element (equations 1 and 2) is the essential reaction as the first step. Termination reactions (3–5) are listed but not limited to the above because recent study has demonstrated that the surface of MXenes can be covalently modified by chlorine, bromine and tellurium. During Al extraction reaction step (equation 1), 1 mol Ti₃AlC₂ produces 1.5 mol H₂. By –F or –OH (equations 3 or 4) termination, 1 mol Ti₃C₂ produce 1 mol H₂, while by –O termination, 1 mol Ti₃C₂ produce 2 mol H₂ (equation 5). Thus, completely transforming 1 mol Ti₃AlC₂ to Ti₃C₂F₂ or Ti₃C₂(OH)₂ produce 2.5 mol H₂, while transforming 1 mol Ti₃AlC₂ to Ti₃C₂O₂ produce 3.5 mol H₂. In accordance with the above results, completely etching 1 mol Ti₃AlC₂ should generate ca. 2.5-3.5 mol H₂ (corresponding to a theoretical H₂ production of about 288–403 cm³ from 1.0 g Ti₃AlC₂ at the temperature of 25 °C). In our experiment, the volume of experimentally collected H₂ ranges from 350 to 380 cm³ per 1.0 g of Ti₃AlC₂ (temperature-dependent), agreeing well with the theoretically prediction. Besides, the O component is estimated to be about 55-80 at.%, and –F/–OH constitute only 20–45 at.% in this etching protocol. Moreover, increasing etching temperature enhances the O termination process, agreeing with our previous study that O terminated Ti₃C₂O₂ is the most stable. Alternatively, the large proportion of O termination in the products confirms the H₂O involvement in etching reaction in aqueous solution, since water-free etching of Ti₃AlC₂ in polar organic solvents results in fluorine-rich MXene.
The energy change of etching Ti₃AlC₂ to Ti₃C₂ in equation 1 is –8.04 eV. While the energy change in etching Ti₃SiC₂ to Ti₃C₂ (equation 2) is only –4.48 eV. The negative reaction energies indicate that both reactions are thermodynamic feasible. The etching of Ti₃SiC₂ to Ti₃C₂ was not successful in the early studies, but was realized via an oxidant-assisted selective etching method to overcome the kinetics, confirming the thermodynamic feasibility. The accumulated electron density between Si and Ti (Fig. 1a) shows that the Si covalently bonds with Ti, while Ti–Al is much weaker. The weak Ti–Al bonds indicate that the Al in Ti₃AlC₂ is easier to be extracted than Si in Ti₃SiC₂. The nature of M–A bonds is coherently correlated with the electronic structures. We compared electronic structures of several typical MAX phases to be etched, i.e. Ti₃SiC₂, Nb₂AlC, Nb₃AlC₃, with Ti₃AlC₂ and Ti₂AlC. Surprisingly, we found that the pseudogaps of A element play key roles in the etching (Supplementary Fig. S1). The underlying physics is that the electronic density of states of A element is closely related to the reactivity. The reactivity of Al element in Ti₃AlC₂ is higher than Si in Ti₃SiC₂ (Fig. 1b), thus the Al is easier to be etched off. Besides, electronic structure evolution during the extraction of A atoms from Ti₃AC₂ MAX phases clearly shows the change of electronic structures (Supplementary Fig. S2).
Fig. 1: Electronic structure of Ti$_3$AlC$_2$ and Ti$_3$SiC$_2$.

**Electron density of Ti$_3$AlC$_2$ and Ti$_3$SiC$_2$ (100) surface** (isosurface is 0.05 e/Å$^3$). **b** Partial density of states and COHP of the Ti–A interface (A=Al, Si). The two MAX phases with identical MX layer but different A element. The M-A bond strength determines the exfoliation possibility.

**Thermodynamics of A extraction and functionalization.** Generally speaking, A is transported along the basal plane. To investigate the A extraction process, we focus on thermodynamics of extracting A out of Ti$_3$AC$_2$ (100) surface to form stable A-containing compounds. Energy profiles of A element extraction was calculated by equations (6-9). **Fig. 2a-b** present the energy profiles of removing Al or Si atoms from the (100) surface to form Ti$_3$C$_2$ MXene and AlF$_3$ or SiF$_4$.

\[
\begin{align*}
2\text{Ti}_3\text{Al}_{n+i}\text{C}_{2n} + 6\text{HF} & = 2\text{Ti}_3\text{Al}_n\text{C}_{2n} + 2\text{AlF}_3 + 3\text{H}_2 \\
\text{Ti}_3\text{Si}_{n+i}\text{C}_{2n} + 4\text{HF} & = \text{Ti}_3\text{Si}_n\text{C}_{2n} + \text{SiF}_4 + 2\text{H}_2 \\
\Delta E (\text{Al}) & = 2E(\text{Ti}_3\text{Al}_n\text{C}_{2n})+2E(\text{AlF}_3)+3E(\text{H}_2)−2E(\text{Ti}_3\text{Al}_n\text{C}_{2n})−6E(\text{HF}) \\
\Delta E (\text{Si}) & = E(\text{Ti}_3\text{Si}_n\text{C}_{2n})+E(\text{SiF}_4)+2E(\text{H}_2)−E(\text{Ti}_3\text{Si}_n\text{C}_{2n})−4E(\text{HF})
\end{align*}
\]
The decreased total energy of the system indicates both Al and Si extractions are thermodynamically feasible process. Intercalation of H$_2$O and HF into the gallery spacing of inorganic layered materials$^{26}$ may lead to termination reaction. Three kinds of H$_2$O/HF coverage models were built to investigate the termination process. Fig. 2c and 2d show 1 monolayer coverage of H$_2$O or HF molecules split on Ti$_3$C$_2$ monolayer respectively. The result demonstrates that low and medium concentration H$_2$O and HF split into adsorbed −O, −F, and −H on Ti$_3$C$_2$ monolayer. Besides, high concentration H$_2$O or HF results in −O or −F termination and H$_2$ gas. The experimentally collected H$_2$ partially comes from H$^+$ reduction by accepting electrons from Al (equation 1), and extra H$_2$ from H$^+$ reduction by accepting electrons from Ti$_3$C$_2$ in the termination process (equation 3-5). Recalling the distinct behaviors of Ti$_3$AlC$_2$ and Ti$_3$SiC$_2$ in hydrofluoric acid, it is reasonable to believe that the extraction of A is the rate-determining step. Extraction of A atoms from MAX phase is the rate-determining step, as the reaction between H$_2$O or HF and Ti$_3$C$_2$ is simultaneous, which will be shown in the following passage.
Fig. 2: Energy profiles of A extraction, and H₂O/HF splitting on Ti₃C₂ monolayer.

a Al extraction from Ti₃AlC₂ to form AlF₃. b Si extraction from Ti₃SiC₂ to form SiF₄. c H₂O interacts with Ti₃C₂ basal surface. d HF interacts with Ti₃C₂ basal surface. The most stable structures of AlF₃ and SiF₄ from Materials Projects are used as reference.²⁷

**Kinetics analysis for etching of MAX phases.** Though the A-extraction reactions in Ti₃AlC₂ and Ti₃SiC₂ are exothermic reaction, the activation energies of the A extraction process is needed to be considered. As shown in Fig. 3, the energy barrier for Al migration from inner site outward along basal plane is calculated to be 0.64 eV in Ti₃AlC₂. This kinetic result is in agreement with previous report²⁸, where the adjacent Al migrates to the edge site in MAX phases. Interestingly, the activation energy based on experiment is coincided about 60 kJ/mol (0.62 eV per molecule). This result also rationalize the collapsed nano arches at edges experimentally observed in Ti₃AlC₂ etched by hydrofluoric acid.²⁹ The energy barrier for Si migration is higher than that of Al, indicates the sluggish kinetics of Si extraction.
Considering the equilibrium in aqueous hydrofluoric acid solution: \( \text{HF}_2^- = \text{HF} + \text{F}^- \), diffusion into the interlayer of Ti\(_3\)AlC\(_2\) was considered for the sake of convenience. To keep charge neutrality in the local environment, atomic F was used in the NEB calculations. Fluorine has the lowest migration barrier in the confined space between the Ti\(_3\)C\(_2\) layers, as evidenced by the NEB results in Fig. 3a. Generally, the atomic migration barrier in Ti\(_3\)AlC\(_2\) increases with increasing atomic radii.\(^{31}\) The fluorine ion migration barrier in Ti\(_3\)SiC\(_2\) is higher than that in Ti\(_3\)AlC\(_2\), due to the smaller interlayer space in Ti\(_3\)SiC\(_2\) (3.96 Å) than that in Ti\(_3\)AlC\(_2\) (4.56 Å, Supplementary Fig. S3). For Ti\(_3\)SiC\(_2\), the Si migration is rather rough without oxidant. Given the oxidant-assistance Ti\(_3\)SiC\(_2\) etching, it is reasonable to propose that Si in the MX interlayer first loses electrons and is oxidized to Si\(^{4+}\) in strong oxidizing circumstance (as evidenced by the high electrostatic potential around Si-Ti bonds, in Supplementary Fig. S4). The Si\(^{4+}\) ionic radius (0.26 Å) is much smaller than Si atomic radius (1.10 Å), thus rendering the Si\(^{4+}\) extraction and sustainable selective etching, which requires further detailed study. The results of transition state calculations are included in Supplementary Fig. S5-11.

**Fig. 3: Kinetics of mass transport at nanolamellar tunnel in MAX phases by NEB.**

![Graphs](image_url)
Energy barriers of atomic species migration in Ti₃AlC₂. Comparison of A outward migration and F inward migration in Ti₃AlC₂ and Ti₃SiC₂. Schematic of A outward migration and F inward migration. Energy minimum path of Al migrates outward and F migrates inward of Ti₃AlC₂ (100) surface. Medium concentration of HF molecules split on Ti₃C₂ monolayer. Medium concentration of H₂O molecules split on Ti₃C₂ monolayer. Note that low and middle concentration H₂O and HF split on Ti₃C₂ monolayer in terms of adsorbed −O, −F, and −H. High concentration H₂O or HF result in −O or −F termination and H₂ gas.

Online monitoring of etching process by gas identification and collection. Using the lab-made gas identification and monitoring devices, the gas produced during etching was identified to be H₂ (see Supplementary Fig. S14-15). Then we studied the etching kinetics of porous Ti₃AlC₂ monolith by using the produced H₂ as an indicator. A set of experiments were performed at varied temperatures, using aqueous HF solution with fixed concentration. To minimize the measurement error that may arise from the highly exothermic reaction and to keep the HF concentration relatively fixed during the entire etching process, excessive HF was used. Fig. 4 presents the hydrogen gas profiles of porous Ti₃AlC₂ monolith exposed to abundant HF solution (50%). Specifically, the volume of H₂ gas evolved at 40 °C was experimentally collected to be 356.8 cm³ at 25 °C. According to overall equations 10-12, the theoretical H₂ volumes are 314.7, 377.7 and 440.6 cm³ at 25 °C, depending on the resultant of Ti₃C₂Tₓ MXene with distinct functional terminations. At the same time, the increased temperature could boost the O termination process and generate more O termination.

\[
\text{Ti}_3\text{AlC}_2 + 3\text{HF} + 2\text{H}_2\text{O} = \text{Ti}_3\text{C}_2(\text{OH})_2 + \text{AlF}_3 + \frac{5}{2}\text{H}_2
\]

\[314.7 \text{ cm}^3 \text{ H}_2 \text{ per gram of Ti}_3\text{AlC}_2\]  

\[
\text{Ti}_3\text{AlC}_2 + 3\text{HF} + 2\text{H}_2\text{O} = \text{Ti}_3\text{C}_2(\text{OH}) + \text{AlF}_3 + 3\text{H}_2
\]

\[377.7 \text{ cm}^3 \text{ H}_2 \text{ per gram of Ti}_3\text{AlC}_2\]  

\[
\text{Ti}_3\text{AlC}_2 + 3\text{HF} + 2\text{H}_2\text{O} = \text{Ti}_3\text{C}_2\text{O}_2 + \text{AlF}_3 + \frac{7}{2}\text{H}_2
\]

\[440.6 \text{ cm}^3 \text{ H}_2 \text{ per gram of Ti}_3\text{AlC}_2\]
(440.6 cm$^3$ H$_2$ per gram of Ti$_3$AlC$_2$)

Then the amount of H$_2$ was used to deduce the possible reaction mechanism. F-terminated reaction is not presented in the reaction equations because –F is isoelectric with –OH. These isoelectric terminations give rise to equal amount of hydrogen. In the case of OH-terminated or F-terminated Ti$_3$C$_2$T$_x$ MXene, the theoretical volume of H$_2$ evolution is only 314.7 cm$^3$ per gram of Ti$_3$AlC$_2$, while the volume approaches as high as 440.6 cm$^3$ per gram of Ti$_3$AlC$_2$ for Ti$_3$C$_2$O$_2$ MXene. The experimentally determined volumes are in the range of these volumes, confirming that the terminations consist of –O and –OH/–F mixture.$^{12}$ This is in line with the well-accepted knowledge on the termination composition of Ti$_3$C$_2$T$_x$ MXene.

**Reaction kinetics analysis.** Etching experiment at four different temperatures shows some common features. As shown in Fig. 4, the H$_2$ evolution profile signifies the overall etching process follows a sigmoidal curve (S-curve). The S-curve has been widely used to model the natural life cycle of many things, from bacteria flora growth, to population growth, and recently found in crystal growth kinetics$^{33}$. The curve is basically a stretched out S shape lying on its side, and can be thought of as having several sections, each of which corresponds to a phase of etching. To quantitatively understand this process, we deduced the possible reaction models (Part II Etching reaction models in Supplementary Information).

We found that neither the conventional reaction-controlled model nor diffusion-controlled model in solid-state reactions can explain the S-shape kinetics curve during the selective etching. Insights can be obtained by combining the H$_2$ evolution curves at four temperatures and their derivative curves. The online gas evolution monitoring data definitely reveals that the etching process includes four well-separated steps: the pre-etching period (stage I), initial etching of the monolith through grain boundary and dissociation of the monolith into individual grains (stage II), burst etching of individual Ti$_3$AlC$_2$ grains (stage III), and completion of the etching (stage IV). Then the experimental data in each stage is used to fit the models and find out the most probable model. The best-fitted models are presented in Fig. 4c.
Fig. 4: Four stages of Ti$_2$AlC$_2$ MAX phase etching reactions.

a. Online H$_2$ monitoring of hydrofluoric acid (40%) etching Ti$_2$AlC$_2$ at 25 °C, 30 °C, 35 °C, 40 °C. b. H$_2$ evolution at 25 °C and its derivative. c. Modeling results and schematic illustration of etching process of MAX phases. Four insets are (I) pre-etching process, (II) induction period, (III) accelerating period, and (IV) completion of etching respectively.

In the pre-etching process (stage I): the solution contacts with the outmost surfaces. The best-fit model is parabolic model which is usually seen in membrane oxidation governed by gas diffusion. The relatively high reaction rate means this is a fast process. The produced H$_2$ in this stage most probably comes from the process that exposed Al atoms are etched off and the outmost Ti layers of Ti$_3$AlC$_2$ particles are functionalized. The reaction between etchant and outmost Al or Ti layers is easy and this process is
controlled by the diffusion of solution. Interestingly, stage II (induction period) follows a linear kinetics at varied temperatures. In this period, the etchant solution comes into the grain boundaries, resembling the siphonage. The best-fitted model is constant liquid-solid interface shift velocity model (Part III in ESI), in which the H₂ amount increases linearly with the liquid-solid interface shift. In this process, the reaction rate is relatively low due to the limited spacing and reactants. Stage III exhibits self-accelerating feature. After the polycrystal divided into small individual grains, each small grain gets full contact with etchants and multilayer Al react with etchants at the same time. This period reflects mainly the intrinsic etching process. The activation energy in this stage corresponds to the intrinsic activation energy of etching reaction. The drastic increase of reaction rate in this period is mainly attributed to the burst of number of Al layers reaction with etchants. The autocatalytic feature was also found in thermo decomposition of transition metal formates and carboxylates.³⁴ Stage IV is the completion of etching.

Quantitive analysis of the reaction rate at the sigmoidal curves reveals the kinetic mechanism.³³ Stage III is selected to determine the activation energy of etching Ti₃AlC₂ grains by HF solution. The Avrami-Erofeev equation was used to fit the III period.

\[-\ln(I-G) = k^2t^2\]  \hspace{1cm} (13)

The dependence of reaction rate constant, \(k\), on the reaction temperature, \(T\), can be described by Arrhenius equation:³³,³⁵

\[k = Ae^{-E_a/RT}\]  \hspace{1cm} (14)

where \(R\), \(A\), and \(E_a\) represent the universal gas constant (8.314 J mol⁻¹ K⁻¹), the frequency factor, and the apparent activation energy, respectively. From the temperature-dependent etching kinetics, the apparent activation energies (\(E_a\)) for the stage III is determined to be 60.17 kJ/mol (Fig. 5b). This is very close to the calculated activation energy of Al migration outward by DFT calculations (61.5 kJ/mol, about 0.64 eV/atom). Again, this result proved that the migration of Al in the interlayer space plays key roles in the etching kinetics.
Fig. 5: Four stages of Ti₃AlC₂ MAX phase etching reactions. Determination of activation energies.

**a** Online H₂ monitoring of hydrofluoric acid (50%) etching HCl-treated Ti₃AlC₂ at 25 °C, 30 °C, 35 °C, and 40 °C. H₂ evolution at 25°C and its derivative are used to indicate the four stages of etching reaction.

**b** Linear fitting of ln(k) as a function of 1/RT, in which the slope of linear regression line can be used to calculate the corresponding reaction activation energy (Eₐ) using the Arrhenius equation. The dotted vertical lines in panel a highlight the typical reaction stages (I, II, III, and IV). Etching process can be accelerated by gentle heating. It has to been admitted that, this study is based on the assumption that the kinetics of gas evolution reflects the kinetics of etching of MAX phases.

**Reaction energy as a descriptor**

Whether a MAX phase can be etched in a certain solution on one hand is related with the structure of the material itself, but on the other hand depends on the etchant. Previous work attributed the successful exfoliation of such materials to the intrinsic weak interlayer bonding, but encouraging communications with experimental colleagues inspired us that the match of materials and etchant may be the key point. Therefore, we selected nearly one hundred typical MAX phases (9 different MX layers and 11 A elements), two main etchants (hydrofluoric acid and hydrochloric acid) in literature and calculated the
reaction energy of etching reactions. After a systematical comparison with available experimental results, we found the reaction energy is an intriguing descriptor of the etching behavior.

**Fig. 6:** Heat maps of reaction energies in etching MAX phases by hydrofluoric and hydrochloric acids.

![Heat maps of reaction energies in etching MAX phases by hydrofluoric and hydrochloric acids.](image)

**a.** Reaction energies of MAX phases and hydrofluoric acid. **b.** Reaction energies of MAX phases and hydrochloric acid. Some experimental results are indicated. The tick √ marks the successful etching and cross × marks the failure of etching.

As shown in **Fig. 6**, the MAX phases with the same A element show similar reaction energies with etchants. The etching possibility mainly depends on the activity of A element, as well as whether A element and etchants can produce stable products. It is found the reaction energy is an easy but effective descriptor to predict the etching possibility. The heat map clearly shows that MAX phases with A=Al or Si are the easiest to be etched in hydrofluoric or hydrochloric acids. Most of the Al-containing MAX phases have been successfully etched by hydrofluoric acid. Mo$_2$AlC could also be etched by hydrofluoric acid if it is synthesized. According to previous experimental work, Mo$_2$C MXenes were synthesized from Mo$_2$Ga$_3$C other than Mo$_2$GaC. This is rationalized by the reaction energies of Mo$_2$GaC and Mo$_2$Ga$_2$C. The former with a positive reaction energy and the latter with a negative one, demonstrating that reaction energy is an effective descriptor, as shown in **Fig. 6**. Moreover, the negative reaction energy of Mo$_2$Ga$_2$C and hydrochloric acid signifying that Mo$_2$Ga$_2$C can also be etched by hydrochloric acid, which has been validated by experiment recently. The HCl-based echant has been successfully used in not only double-
Ga MAX phases but also in Al-containing MAX phases. Etching Si-containing MAX phases by hydrofluoric acid is feasible based on the reaction energy and this has been realized by an oxidation-assistant selective etching method. Experimental trials to etch Ti$_2$SC by hydrofluoric acid result in not Ti$_2$C MXene but sulfur carbide SC$_x$ nanosheet. Interestingly, the results here clearly shows that the transformation of Ti$_2$SC to Ti$_2$C MXene in hydrofluoric acid is thermodynamically unfavorable. As is shown, reaction energy is a convenient descriptor of etching possibility with robustness.

**Discussion**

In summary, we have elucidated the mechanism of topochemical reaction of preparing Ti$_3$C$_2$T$_x$ MXene from Ti$_3$AlC$_2$ precursor in hydrofluoric acid by means of a combination of DFT calculations and operando observation. The etching possibility mainly depends on the activity of A element, and whether A element and etchants can produce stable products. The topochemical reaction shows a sigmoidal reaction curve, following typical self-accelerating reaction kinetics and the reaction activation energy is determined to be 60 kJ/mol. Reaction between Al atoms and hydrofluoric acid solution in the confined interlayer space between Ti$_3$C$_2$ layers is the rate-limiting step. Reaction energy derived from thermodynamics is a convenient descriptor of etching possibility with remarkable robustness. This descriptor can not only rationalize most of the experimental results in the literature and but also predict potential etchants efficiently. The results obtained in the present study are of reference and guiding significance to the rational design and topochemical transformation of layered materials into MXenes and other 2D materials.

**Methods**

**Synthesis of Porous Ti$_3$AlC$_2$ Monolith.** The porous Ti$_3$AlC$_2$ monolith (porosity, ~40%) used in this work was prepared in the authors’ laboratory by the solid–liquid reaction synthesis method. The synthesis procedure adopted is in consistent with the earlier work. The prepared porous monolith is phase-pure as determined by X-ray diffraction (XRD) examination.
**Real-Time Gas Evolution Monitoring.** Ti$_3$AlC$_2$ and HF acid aqueous solution react in the reactor I as shown in the diagram (see Supplementary Fig. 14). Reactor I using the cork processed by PTFE rod and body of bottle made of PET, has been proven good air-tightness during experiments. The Reactor I needs to react in constant temperature, so it is put in a water bath 5. The generated gas of reaction passes through a Teflon tube into a filter to remove HF volatilized from Reactor I. HF filter II is equipped with the concentration of 1mol/L in the aqueous solution of NaOH. While the filtered gas is discharged into the transparent gas collecting bottle III, the water of the bottle is discharged in the liquid collector IV. The liquid collector IV has a very small opening to prevent the liquid from volatilization during the long time test. In order to ensure that the gas pressure above the water in gas collecting bottle III is kept at a pressure, the gas collecting bottle III is arranged on the platform of Automatic elevator4. When the laser is block by the float and laser receiver cannot receive laser, optical inductive switch is disconnected and elevator do not move. While the liquid level of the gas collecting bottle IV drops, the laser reaches the laser receiver through the transparent gas collecting bottle III, and optical inductive switch is connected, and the platform of Automatic elevator4 is lift. After slightly descending, the laser is on the surface of the float block again, and elevator stop downward movement at the same time. Automatic elevator4 always ensures the liquid level in gas collecting bottle III is lower than that of the liquid outlet for a fixed small distance we set before the experiment. By the means, the gas above the liquid pressure keeps a standard atmospheric pressure and the discharge volume of water and the molar amount of the gas have a linear relationship. Gas collecting bottle III is placed in the balance 3, which can record the quality once every two seconds. Meanwhile, the data is input into the computer. Through this set of platform, we can accurately measure the time and the Ti$_3$AlC$_2$ and HF acid aqueous solution reaction gas production curve. In every experiment, we use three pieces of samples, which size is about 2 mm × 8 mm × 15 mm and get the curve about gas production and time.
**DFT Computation.** The density functional theory (DFT) computations were performed by using the plane-wave technique as implemented in the Vienna ab initio simulation package (VASP). The ion–electron interaction is described with the projector augmented wave (PAW) method. A 500 eV cutoff was used for the plane-wave basis set. The exchange correlation energy is described by the functional of Perdew, Burke, and Ernzerhof (PBE). The geometry optimizations were performed by using the conjugated gradient method, and the convergence threshold was set to be $10^{-4}$ eV in energy and 0.1 eV/Å in force. The Brillouin zone was represented by Monkhorst–Pack special k-point mesh of $5 \times 5 \times 1$ for geometry optimizations. To investigate the splitting of H$_2$O on the Ti$_3$C$_2$ monolayers, three kinds of supercells was considered. A $3 \times 3 \times 1$, a $\sqrt{3} \times \sqrt{3} \times 1$ and a $1 \times 1 \times 1$ supercell with one adsorbed H$_2$O were used, and the PBE-D method, which introduces dispersion interactions by using an empirical potential of the form $C_6R$, was adopted. Furthermore, the climbing-image nudged elastic band (CI-NEB) method implemented in VASP was used to determine the diffusion energy barrier and the minimum energy pathways for splitting of H$_2$O on the Ti$_3$C$_2$ surfaces. This method involves optimizing a chain of images that connect the initial and final state. Each image is allowed to move only in the direction perpendicular to the hyper tangent. Hence, the energy is minimized in all directions except for the reaction path.

**Data Availability**

The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information files. All of the other data are available from the corresponding author upon reasonable request.

**Code Availability**

The computational codes used in this work are available from the corresponding author on reasonable request.

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**Competing interests**
The authors declare no competing interests.

**Supplementary Information**
Supplementary Information. The online version contains supplementary material available at https://doi.org/.

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Electronic Supplementary Information for

Unveiling the spontaneous conversion of layered MAX phases to 2D MXenes

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Supplementary summary

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Part I: Supplementary Figures

**Fig. S1** Electronic structure of A atoms in Ti$_2$AlC, Ti$_3$AlC$_2$, Nb$_2$AlC, Nb$_4$AlC$_3$, and Ti$_3$SiC$_2$. Pseudogap widths of A in MAX phases are indicated and generally in order of etching difficulty.
Fig. S2 Electronic structure evolution during the extraction of A atoms from Ti$_3$AC$_2$ MAX phases.
**Fig. S3** Interlayer spacing in (a) Ti$_3$AlC$_2$ and (b) Ti$_3$SiC$_2$.

**Fig. S4.** Electrostatic potential at a Ti$_3$AlC$_2$(100), b Ti$_3$SiC$_2$(100), c Ti$_2$AlC(100), b Ti$_3$GeC$_2$(100). The potential at Ti-Al bond is higher and closer to $E_{\text{vac}}$, indicating the electrons around Ti-Al bonds are easier to be transferred.
Fig. S5 Energy profiles of H$_2$O/HF splitting on Ti$_3$C$_2$ monolayer. (a) low concentration, (b) middle concentration and (c) high concentration of H$_2$O molecules split on Ti$_3$C$_2$ monolayer. (d) low concentration, (e) middle concentration and (f) high concentration of HF molecules split on Ti$_3$C$_2$ monolayer. Note that low and middle concentration H$_2$O and HF split on Ti$_3$C$_2$ monolayer in terms of adsorbed O, F, and H. High concentration H$_2$O or HF result in O or F termination and H$_2$ gas.

Fig. S6 The energy barrier of Al atom migration along the interlayer tunnel without termination.
Fig. S7 The energy barrier of Al atom migration along the interlayer tunnel with O termination.

Fig. S8 The energy barriers of F\(^-\) ion migration along tunnel into the Ti\(_3\)AlC\(_2\) interlayer. The unique penetrating ability of F\(^-\) is the key factor in the etching process.
Fig. S9 The energy barriers of $\text{F}^-$ ion migration along tunnel into the $\text{Ti}_3\text{SiC}_2$ interlayer. The unique penetrating ability of $\text{F}^-$ is the key factor in the etching process.

Fig. S10 The energy barriers of $\text{H}^+$ ion migration along the interlayer tunnel into the interlayer.
Fig. S11 The energy barriers of Cl\textsuperscript{-} ion migration along the tunnel into the interlayer.

Fig. S12 Electronic structure of A atoms in Mo\textsubscript{2}Ga\textsubscript{2}C, and Mo\textsubscript{2}GaC. Mo\textsubscript{2}Ga\textsubscript{2}C with smaller pseudogaps has been successfully etched by hydrochloric acid while Mo\textsubscript{2}GaC has not yet.
Fig. S13 Work functions of Ti$_3$AlC$_2$ (100) and Ti$_3$SiC$_2$ (100). The work function of Ti$_3$AlC$_2$ (100) is about 0.5 eV smaller than that of Ti$_3$SiC$_2$ (100). The trend is in agreement with earlier studies that corrosion behavior of metal can be correlated with work function. However, using work function as a descriptor of etching in MAX phases with anisotropic bonding character would be with caution. As the work function of a certain surface is the average of local potential, the more negative Al proportion would increase the calculated work function. For example, calculated work function of Ti$_2$AlC (100) is 5.65 eV, which is even larger than that of Ti$_3$SiC$_2$ (100). Therefore, the bond-specific local potential is more meaningful for corrosion of materials with anisotropic bonding character.
Fig. S14 Schematic illustration of the online gas evolution monitoring equipment.

Fig. S15 Mass spectrum for the determination of released gases collected in the etching reaction.
Fig. S16 Etching reactions of Ti₃AlC₂ MAX phase at different temperature can be divided into four stages. Online H₂ monitoring of hydrofluoric acid (40%) etching Ti₃AlC₂ and its derivative at a 25 °C, b 30 °C, c 35 °C, and d 40 °C.
Fig. S17 Comparison of experimentally collected data and modeling results. a Experimentally collected gas evolution data of Ti$_3$AlC$_2$ emerging in 40% HF aqueous solution at 25°C. b Modeling results and schematic illustration of etching process of MAX phases. (I) Pre-etching process. (II) Induction period. (III) Accelerating period (burst etching). (IV) Completion of etching.
Fig. S18 Etching reactions of HF-treated Ti$_3$AlC$_2$ MAX phase at different temperature can be divided into four stages. Online H$_2$ monitoring of hydrofluoric acid (50%) etching HCl-treated Ti$_3$AlC$_2$ and its derivative at a 25 °C, b 30 °C, c 35 °C, d 40 °C.
### Part II: Supplementary Tables

**Table S1.** Atomic radii$^1$ and ionic radii$^2$ of H, F, Cl, Al and Si

| Atomic species | Atomic radius (pm) | Ionic radius (pm) |
|----------------|--------------------|-------------------|
| H              | 25                 | -4                |
| F              | 50                 | 128               |
| Cl             | 100                | 181               |
| Al             | 125                | 39                |
| Si             | 110                | 26                |

**Table S2.** Reaction energies of MAX phases with HF

|        | $\text{M}_2\text{X}$ | $\text{M}_3\text{X}_2$ | $\text{M}_4\text{X}_3$ |
|--------|------------------------|------------------------|------------------------|
| A      |                         |                        |                        |
| Al     | -7.85 -7.15-7.43-6.92 | -8.04 -8.25-7.25-7.39 | -7.34                  |
| Ga     | 1.39 1.73 1.38 1.56   | 1.23 1.16 1.76 1.54   | 1.47                   |
| Ga$_2$ | -3.54 -2.91 -3.18 -2.69 | -3.62 -4.28 -3.13 -3.28 | -3.12                   |
| In     | 1.70 1.84 1.03 1.47   | 1.53 1.92 1.57 1.78   | 1.50                   |
| Tl     | 6.88 6.70 5.83 6.09   | 6.69 7.28 6.40 6.60   | 6.16                   |
| Si     | -4.23 -4.01 -4.36 -4.41 | -4.48 -4.55 -4.48 -4.89 | -4.93                   |
| Ge     | 4.79 4.66 4.09 4.12   | 8.65 4.79 4.35 3.91   | 3.62                   |
| Sn     | 2.35 2.07 1.21 1.69   | 6.57 2.86 1.50 1.56   | 0.96                   |
| Pb     | 7.97 7.55 6.75 6.98   | 7.74 8.71 6.76 7.07   | 6.34                   |
| P      | 4.77 5.21 4.27 3.30   | 4.34 5.28 4.29 4.28   | 4.21                   |
| As     | 10.38 10.49 9.46 8.92 | 9.96 10.89 9.57 9.48   | 9.14                   |
| S      | 18.84 17.30 16.49 15.00 | 18.31 19.44 17.34 16.39 | 15.78                   |

**Table S3.** Reaction energies of MAX phases with HCl

|        | $\text{M}_2\text{X}$ | $\text{M}_3\text{X}_2$ | $\text{M}_4\text{X}_3$ |
|--------|------------------------|------------------------|------------------------|
| A   | Ti$_2$C | Nb$_2$C | V$_2$C | Mo$_2$C | Ti$_3$C$_2$ | Zr$_3$C$_2$ | Ti$_4$N$_3$ | Nb$_4$C$_3$ | Ta$_4$C$_3$ |
|-----|---------|---------|--------|---------|------------|------------|------------|------------|------------|
| Al  | -1.40   | -0.70   | -0.98  | -0.47   | -1.59      | -1.80      | -0.80      | -0.94      | -0.89      |
| Ga  | 2.28    | 2.62    | 2.27   | 2.45    | 2.12       | 2.05       | 2.65       | 2.43       | 2.36       |
| Ga$_2$ | -1.76 | -1.13   | -1.40  | -0.91   | -1.84      | -2.50      | -1.35      | -1.50      | -1.34      |
| In  | 2.46    | 2.59    | 1.78   | 2.22    | 2.28       | 2.67       | 2.33       | 2.53       | 2.25       |
| Tl  | 4.49    | 4.32    | 3.45   | 3.71    | 4.31       | 4.90       | 4.01       | 4.22       | 3.77       |
| Si  | 0.57    | 0.80    | 0.44   | 0.40    | 0.33       | 0.26       | 0.33       | -0.09      | -0.13      |
| Ge  | 4.12    | 3.98    | 3.42   | 3.44    | 7.98       | 4.11       | 3.67       | 3.24       | 2.95       |
| Sn  | 3.11    | 2.83    | 1.97   | 2.45    | 7.33       | 3.62       | 2.26       | 2.32       | 1.75       |
| Pb  | 5.21    | 4.79    | 3.98   | 4.22    | 4.98       | 5.95       | 3.99       | 4.30       | 3.58       |
| P   | 9.48    | 9.92    | 8.98   | 8.02    | 9.05       | 10.00      | 9.00       | 8.99       | 8.92       |
| As  | 10.33   | 10.44   | 9.41   | 8.86    | 9.91       | 10.84      | 9.52       | 9.42       | 9.09       |
| S   | 11.02   | 9.48    | 8.67   | 7.18    | 10.49      | 11.62      | 9.52       | 8.57       | 7.96       |
# Part III: Etching reaction models

**1. Reaction-controlled**

| 3D | 1.1 F-sphere |
|----|--------------|
|    | \((1 - G)^{\frac{2}{3}} - 1 = \frac{8}{3} \pi KR_0^2 t\) |

|    | 1.2 \(n\) particles react simultaneously |
|----|----------------------------------------|
|    | \((1 - G)^{\frac{2}{3}} = \frac{8}{3} \pi KR_0^2 \left[ \frac{1}{3} t^3 - c_1 t^2 + (c_1^2 + c_2) t \right] + 1\) |

|    | 1.3 F-constant |
|----|---------------|
|    | \(\ln(1 - G) = -Kt\) |

| 2D | 1.4 F-round plate |
|----|-------------------|
|    | \((1 - G)^{\frac{1}{2}} - 1 = K' t\) |

|    | 1.5 \(n\) layers react simultaneously |
|----|-------------------------------------|
|    | \(\frac{1}{\sqrt{1 - G}} = \frac{\pi KR_0}{\frac{1}{3} t^3 - c_1 t^2 + (c_1^2 + c_2) t} + 1\) |

|    | 1.6 F-constant |
|----|---------------|
|    | \(\ln(1 - G) = -Kt\) |

**2. Diffusion-controlled**

| 3D | 2.1 Jander’s sphere model |
|----|---------------------------|
|    | \([1 - (1 - G)^{\frac{1}{3}}]^2 = \frac{K}{R_0^2} t\) |

|    | 2.2 Ginsterlinger’s sphere model |
|----|---------------------------------|
|    | \(1 - \frac{2}{3} G - (1 - G)^{\frac{2}{3}} = K' t\) |

|    | 2.3 Ginsterlinger’s cylinder model |
|----|----------------------------------|
|    | \(\ln(1 - G) \cdot (1 - G) + G = \frac{4K'}{R_0^2 t}\) |

| 2D | 2.4 Plate model |
|----|-----------------|
|    | \([1 - (1 - G)^{\frac{1}{3}}]^2 = \left(\frac{K}{R_0}\right)^2 t\) |

|    | 2.5 Round plate model |
|----|-----------------------|
|    | \(2(1 - G)^{\frac{3}{2}} - 3(1 - G) + 1 = K' t\) |

|    | 2.6 Constant interface shift velocity |
|----|--------------------------------------|
|    | \(1 - (1 - G)^{\frac{1}{3}} = K' t\) |
For solid state reactions encompassing diffusion and chemical reactions, the reaction rate of total reaction $v$, diffusion rate $v_D$, and chemical reaction rate $v_R$ follow the relationship,

\[
\frac{1}{v} = \frac{1}{v_R} + \frac{1}{v_D}
\]

The total reaction rate is determined by the slowest process. The rate of reaction and diffusion are expressed as the following equations respectively:

\[
v_R = k_c
\]

\[
v_D = D \frac{dc}{dx} = D \frac{c_0 - c}{\delta}
\]

When the process reaches an equilibrium,

\[
v = v_R = v_D
\]

\[
k_c = D \frac{c_0 - c}{\delta}
\]

The etching of layered compounds is the reaction between solid and liquid, belongs to the general solid state reaction. Suppose that supplying the etchants, HF and H$_2$O in great excess relative to the precursor to ensure that the concentration of the etchant would mainly remain as a constant throughout the reaction. Under such assumption, the rate can be described as following:

\[
rate = \frac{d[MXene]}{dt} = k[\text{MAX}][\text{etchant}] = k[\text{MAX}]
\]

the reaction rate $\frac{dG}{dt}$ is dependent on the unreacted MAX phases $(1-G)$.

\[
\frac{dG}{dt} = KF(1-G)^n
\]

1. Reaction-controlled

\[
\frac{dG}{dt} = KF(1-G)^n \quad (S1)
\]
$G$ is the reacted part, $t$ is the reaction time, $k$ is the reaction rate constant, $F$ is the reaction interface, $n$ is the reaction order. Assuming the reaction happens at the unreacted part $(1-G)$, while the reacted part $(G)$ does not contribute to the reaction rate. Considering only the first-order reaction $(n=1)$, then

$$\frac{dG}{dt} = KF(1-G) \quad (S2)$$

1.1 $F$-sphere

![3D sphere](image)

$$G = \frac{V}{V_0} = \frac{\frac{4}{3}\pi R_0^3 - \frac{4}{3}\pi (R_0 - x)^3}{\frac{4}{3}\pi R_0^3} = \frac{R_0^3 - (R_0 - x)^3}{R_0^3}$$

$$F = 4\pi (R_0 - x)^2 = 4\pi R_0^2 (1-G)^{\frac{2}{3}}$$

$$\frac{dG}{dt} = KF(1-G) = 4\pi R_0^2 K(1-G)^{\frac{5}{3}}$$

$$(1-G)^{\frac{2}{3}} - 1 = 4\pi R_0^2 Kt$$

1.2 Considering one polycrystalline Ti$_3$AlC$_2$ particle divided into $n$ nanocrystal particle.
\[
G = \frac{V}{V_0} = \frac{\frac{4}{3} \pi R_n^3 - \frac{4}{3} \pi (R_n - x)^3}{\frac{4}{3} \pi R_n^3 \cdot n} = \frac{R_n^3 - (R_n - x)^3}{R_n^3} = 1 - \left(1 - \frac{x}{R_n}\right)^3
\]

\[
F = 4 \pi (R_n - x)^2 \cdot n = n \cdot 4 \pi R_n^2 \left(1 - \frac{x}{R_n}\right)^2 = 4 \pi n R_n^2 \left(1 - G\right)^3
\]

For first order reaction,

\[
\frac{dG}{dt} = K F (1 - G) = K \cdot 4 \pi n R_n^2 \left(1 - G\right)^3 \cdot (1 - G) = K \cdot 4 \pi n R_n^2 \left(1 - G\right)^5
\]

\[
n \cdot \frac{4}{3} \pi R_n^3 = \frac{4}{3} \pi R_0^3
\]

\[
R_n = n^{-\frac{1}{3}} R_0
\]

\[
\frac{dG}{dt} = K \cdot 4 \pi n R_n^2 \left(1 - G\right)^5 = K \cdot 4 \pi n \cdot n^{-\frac{2}{3}} R_0^2 \left(1 - G\right)^5 = 4 \pi Kn^3 R_0^2 \left(1 - G\right)^5
\]

(1) In the situation that the particle number is the function of time, and given by \( n = ct \)

\[
\frac{dG}{dt} = 4 \pi Kn^3 R_0^2 \left(1 - G\right)^5 = 4 \pi K c^3 t^3 R_0^2 \left(1 - G\right)^5
\]

\[
(1 - G)^3 \frac{dG}{dt} = 4 \pi K c^3 R_0^2 t^3 dt
\]

\[
\frac{3}{2} (1 - G)^{-\frac{2}{3}} = 4 \pi K c^3 R_0^2 t^3 \cdot \frac{3}{4} + C
\]

\[
t = 0, G = 0
\]

\[
C = \frac{3}{2}
\]

\[
(1 - G)^{-\frac{2}{3}} = 2 \pi K c^3 R_0^2 t^3 + 1
\]

(2) In the situation that the particle number is given by
\[ n = (t - c_1)^2 + c_2 \]
\[ \frac{dG}{dt} = 4\pi K [(t - c_1)^2 + c_2] R_0^2 \left( 1 - G \right)^{\frac{5}{3}} \]
\[ (1 - G)^{-\frac{2}{3}} dG = 4\pi K R_0^2 [(t - c_1)^2 + c_2] dt \]
\[ (1 - G)^{-\frac{2}{3}} = \frac{8}{3} \pi K R_0^2 \left[ \frac{t^3}{3} - c_1 t^2 + (c_1^2 + c_2) t \right] + 1 \]
\[ G = 1 - \left\{ \frac{8}{3} \pi K R_0^2 \left[ \frac{t^3}{3} - c_1 t^2 + (c_1^2 + c_2) t \right] + 1 \right\}^{-\frac{3}{2}} \]
\[ c_1 = 1, c_2 = 0.1, \frac{8}{3} \pi K R_0^2 = 0.1 \]
\[ G = 1 - \left\{ 0.1 \left[ \frac{t^3}{3} - t^2 + 1.1 t \right] + 1 \right\}^{-\frac{3}{2}} \]

The \( G-t \) is plot as

### 1.3 \( F \)-constant (3D)

\[ \frac{dG}{dt} = KF (1 - G) = K' (1 - G) \]
\[ - \ln(1 - G) = K't \]
1.4 \( F \)-round plate model:

\[
\begin{align*}
G &= 1 - \frac{S}{S_0} = 1 - \frac{\pi (R_0 - x)^2}{\pi R_0^2} = 1 - \frac{(R_0 - x)^2}{R_0^2} \\
F \text{ is a function of } G: \quad F &= 2\pi (R_0 - x) = 2\pi R_0 (1 - G)^{\frac{3}{2}} \\
\frac{dG}{dt} &= KF (1 - G) = 2\pi K R_0 (1 - G)^{\frac{3}{2}} \\
2(1 - G)^{-\frac{1}{2}} &= 2\pi K R_0 t + 2 \\
2\pi K R_0 &= K^* \\
(1 - G)^{-\frac{1}{2}} - 1 &= K^* t
\end{align*}
\]

When \( K^* = 1 \)
1.5 $n$ layers react at the same time

For 2D round plate model

$$G = 1 - \frac{S}{S_0} = 1 - \frac{\pi (R_0 - x)^2}{\pi R_0^2} = 1 - \frac{(R_0 - x)^2}{R_0^2}$$

$F$ is a function of $G$: $F = 2\pi (R_0 - x) = 2\pi R_0 (1 - G)^{\frac{1}{2}}$

For reactions of $n$ layers are initiated at the same time,

$$\frac{dG}{dt} = nKF (1 - G) = 2\pi nKR_0 (1 - G)^{\frac{3}{2}}$$

(1) For $n = ct$

$$(1 - G)^{\frac{3}{2}} \frac{dG}{dt} = 2\pi KR_0 c dt$$

$$2(1 - G)^{\frac{1}{2}} = \pi KR_0 c t^2 + 2$$

$$G = 1 - \frac{4}{(2 + \pi KR_0 c t^2)^2}$$

$$\frac{d^2 G}{dt^2} = \pi KR_0 c \frac{d}{dt} \left[ t (1 - G)^{\frac{3}{2}} \right]$$

$u = t, v = (1 - G)^{\frac{3}{2}}$

$$(uv)' = u'v + uv' = (1 - G)^{\frac{3}{2}} - \frac{3}{2} (1 - G)^{\frac{1}{2}} t \left[ 2\pi KR_0 c t (1 - G)^{\frac{3}{2}} \right] = (1 - G)^{\frac{3}{2}} \left[ 1 - 3\pi KR_0 c (1 - G)^{\frac{1}{2}} t^2 \right]$$

$$1 - 3\pi KR_0 c (1 - G)^{\frac{1}{2}} t^2 = 1 - 3(1 - G)^{\frac{1}{2}} \left( \frac{2}{\sqrt{1-G}} - 2 \right) = 6\sqrt{1-G} - 5$$

$$0 < G < 0.31, (uv') > 0, \frac{d^2 G}{dt^2} > 0$$

$$0.31 < G < 1, (uv') < 0, \frac{d^2 G}{dt^2} < 0$$
(2) For $n = (t-c_1)^2 + c_2$

$$\frac{dG}{dt} = n \cdot 2\pi KR_0 (1-G)^{\frac{3}{2}} = 2\pi KR_0 [(t-c_1)^2 + c_2] (1-G)^{\frac{3}{2}}$$

$$\int (1-G)^{-\frac{1}{2}} dG = \int 2\pi KR_0 [(t-c_1)^2 + c_2] dt$$

$$2(1-G)^{-\frac{1}{2}} = 2\pi KR_0 \left[ \frac{1}{3} - c_1 t^2 + (c_1^2 + c_2) t + c_3 \right]$$

$t = 0, G = 0, c_3 = \frac{1}{2\pi KR_0}$

$$\frac{1}{\sqrt{1-G}} = \pi KR_0 \left[ \frac{1}{3} - c_1 t^2 + (c_1^2 + c_2) t \right] + 1$$

$c_2 = 0, n = (t-c_1)^2$

$$\frac{1}{\sqrt{1-G}} = \pi KR_0 \left[ \frac{1}{3} - c_1 t^2 + c_1^2 t \right] + 1$$

$$G = 1 - \frac{1}{[\pi KR_0 \left( \frac{1}{3} - c_1 t^2 + c_1^2 t \right) + 1]^2}$$

$$\pi KR_0 = K'$$

$$G = 1 - \frac{1}{[K' \left( \frac{1}{3} - c_1 t^2 + c_1^2 t \right) + 1]^2}$$
1.6 $F$-constant (2D)

\[
\frac{dG}{dt} = KF(1 - G) = K_1(1 - G)
\]

\[- \ln(1 - G) = K_1t\]

2. Diffusion-controlled
According to the Fick’s law,

\[ \frac{dm}{dt} = D \left( \frac{dc}{dx} \right)_{x=x_0} \]

**2.1 Jander’s sphere model**

\[ G = \frac{V}{V_0} = \frac{4}{3} \pi R_0^3 - \frac{4}{3} \pi (R_0 - x)^3 = \frac{R_0^3 - (R_0 - x)^3}{R_0^3} \]

\[ x = R_0 [1 - (1 - G)\frac{1}{3}] \]

According to Jander’s model, \( x^2 = Kt \)

\[ x^2 = R_0^2 \left[ 1 - (1 - G)\frac{1}{3} \right]^2 = Kt \]

\[ \left[ 1 - (1 - G)\frac{1}{3} \right]^2 = \frac{K}{R_0^2} t = K't \]

**2.2 Ginsterlinger’s sphere model**
According to Ginsterlinger’s model,
\[
\frac{dx}{dt} = K_0 \frac{R_0}{x(R_0 - x)}
\]

\[
1 - \frac{2}{3}G = (1 - G)^{\frac{2}{3}} = K't
\]

2.3 Ginsterlinger’s cylinder model

\[
dV = [\pi(R_0 - x)^2(h_0 - x)] - [\pi(R_0 - x - dx)^2(h_0 - x - dx)]
\]

\[
dV = \pi[3x^2 - (4R_0 + 2h_0)x + R_0^2 + 2R_0h_0]dx
\]

\[
\frac{dm}{dt} = \rho \frac{dV}{dt} = \rho \pi[3x^2 - (4R_0 + 2h_0)x + R_0^2 + 2R_0h_0]dx = D \frac{c_0}{x}
\]

\[
G = 1 - \frac{V_1}{V_0} = 1 - \frac{\pi(R_0 - x)^2(h_0 - x)}{\pi R_0^2 h_0} = 1 - (1 - \frac{x}{R_0})^2 (1 - \frac{x}{h_0})
\]

\[
\ln(1 - G) \cdot (1 - G) + G = K't
\]
2.4 Plate model

For Jander’s diffusion model, the $x$ is proportional to the $\frac{1}{t^2}$ in diffusion process

$$x = K_1 t^2$$

$$G = 1 - (1 - \frac{K_1}{R_0} t^2)^2$$

$$\frac{K_1}{R_0} = K'$$

$$G = 1 - (1 - K' t^2)^2$$
2.5 Round plate model

\[ dm = 2\pi(R_0 - x)\rho dx \]

According to the Fick’s law,

\[ \frac{dm}{dt} = D \frac{dc}{dx} \bigg|_{x=\xi} \]

\[ \frac{dx}{dt} = \frac{D}{2\pi\rho(R_0 - x)} \frac{dc}{dx} \bigg|_{x=\xi} \]

\[ \frac{dc}{dx} \bigg|_{x=\xi} = \frac{c_0}{x} \]

\[ \frac{dx}{dt} = \frac{D}{2\pi\rho(R_0 - x)} \frac{c_0}{x} = \frac{Dc_0}{2\pi\rho x(R_0 - x)} \]

\[ K_1 = \frac{Dc_0}{2\pi\rho} \]

\[ x(R_0 - x)dx = K_1 dt \]

\[ t = 0, x = 0 \]

\[ \frac{R_0}{2} x^2 - \frac{1}{3} x^3 = K_1 t \]

\[ G = 1 - \frac{(R_0 - x)^2}{R_0^2} \]

\[ x = R_0(1 - \sqrt{1 - G}) \]

\[ 2(1 - G)^{\frac{3}{2}} - 3(1 - G) + 1 = \frac{6K_1}{R_0^3} t \]

\[ K' = \frac{6K_1}{R_0^3} = \frac{3Dc_0}{\pi\rho R_0^3} \]

\[ 2(1 - G)^{\frac{3}{2}} - 3(1 - G) + 1 = K' t \]
2.6 Constant velocity of reaction interface shift

The liquid-solid interface shift with constant velocity.

\[
\frac{dx}{dt} = v
\]
(1) For 2D one-way etching process,

\[ x = vt \]

\[ G = \frac{vt \cdot a}{ab} = \frac{v}{b} \]

\[ \frac{v}{b} = K' \]

\[ G = K't \]

(2) For 2D round plate, \( x = vt \), \( v \) is the velocity of reaction interface shift.

\[ G = 1 - \frac{\pi (R_0 - x)^2}{\pi R_0^2} = 1 - \frac{(R_0 - vt)^2}{R_0^2} = 1 - (1 - \frac{v}{R_0})^2 \]

\[ \sqrt{1-G} = 1 - \frac{v}{R_0}t \]

\[ 1 - \sqrt{1-G} = \frac{v}{R_0}t = K't \]
For the etching reaction, in the first stage (stage I), the diffusion on the surface is fast \( (v_D \text{ is large}) \), and the surface reaction rate \( v_R \) controlled the total reaction. Then in stage II, the diffusion of A atom is the lowest step in the etching process, and controlled the total reaction. In stage III, the number of etching sites increase drastically and the etching shows a self-accelerating characteristic. This is also observed in thermal decomposition. Avrami-Erofeev equation\(^3\) is usually employed to describe the self-accelerating reaction.

\[
[-\ln(1-G)]^n = kt, n = \frac{1}{2}, \frac{1}{3}
\]

Where \( n = \frac{1}{2} \) and \( n = \frac{1}{3} \) corresponds to two- and three-dimensional reaction respectively. The drawback of the Avrami-Erofeev equation used in etching reaction is that it does not consider the influence of etchant in aqueous environment.

**The deduction of parabolic kinetics**

For membrane with thickness \( y \), the parabolic relationship of kinetics is deduced as following,

\[
\frac{dy}{dt} = \frac{k_p}{y} \\
\int y dy = \int k_p dt \\
y^2 = 2k_p t + c
\]

With the increase of membrane thickness, the diffusion of reactant through the membrane is decreased. The reaction rate is inverse ratio with the membrane thickness.

**The deduction of Avrami-Erofeev equation\(^3\)**

For a reaction with a constant number of nuclei per unit length \( (N) \), or when at the beginning of the reaction a constant number of nuclei is formed immediately (site saturation), and assuming one-dimensional growth, the reaction rate is given by

\[
\frac{dG}{dt} = Nk
\]
To take overlap of nuclei into account, the right-hand side of equation must be multiplied by \((1-G)\)

\[
\frac{dG}{dt} = Nk(1-G)
\]

Integration results in

\[-\ln(1-G) = \int Nk dt = \int k_g dt\]

For isothermal reactions \(k_g\) is constant, hence

\[-\ln(1-G) = k_g t\]

If nuclei grow isothermally in two dimensions with an equal rate constant for each dimension, and allowing for overlap

\[-\ln(1-G) = C_2 N_2 \left[ \int k_i dt \right]^2 = k_g^2 t^2\]

If nuclei grow isothermally in three dimensions with an equal rate constant for each dimension, and allowing for overlap

\[-\ln(1-G) = C_3 N_3 \left[ \int k_i dt \right]^3 = k_g^3 t^3\]

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