



Opportunities of MXenes in Heterogeneous Catalysis: V₂C as Aerobic Oxidation Catalyst

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MXenes are two-dimensional nanomaterials having alternating sheets of one atom-thick early transition metal layer and one atom-thick carbide or nitride layer. The external surface contains termination groups, whose nature depends on the etching agent used in the preparation procedure from the MAX phase. The present *concept* proposes that, due to their composition, the metal-surface termination groups make MXenes particularly suited as heterogeneous catalysts for some reactions. This proposal comes from the consideration that early transition metal atoms bonded to hydroxyl and oxo groups are a general type of active sites in heterogeneous catalysis and that similar catalytic centers can also be present in the MXene structure. After having presented the concept, we have selected V₂C MXene as an example to illustrate its catalytic activity and

to show how the catalytic performance varies when the surface groups are modified. As a test reaction, we selected the aerobic oxidation of indane to the corresponding indanol/indanone mixture using molecular oxygen as terminal oxidizing reagent. Two previously reported procedures to modify the surface groups, namely surface dehydroxylation by thermal treatment under diluted hydrogen flow and surface oxidation with ammonium persulfate to convert some surface groups into oxo groups were used, observing in both cases a decrease in the catalytic activity of V₂C. Based on this, V^{III/IV}-OH are proposed as catalytic centers in this aerobic oxidation. Overall, the present *concept* shows the merits of MXenes in heterogeneous catalysis, based on their chemical composition and the surface functionality.

1. Introduction

MXenes are two-dimensional (2D) nanomaterials constituted by the stacking of one atom-thick layers of early transition metals ("M" in the formula) alternating with one atom-thick carbide or nitride layer ("X" in the formula).^[1] The surface metal atoms are bonded to termination groups ("T" in the formula), such as -F, -O, -OH or -Cl, that are implanted during MXene synthesis. The transition metal layers are always external and for this reason general MXene formula is M_{n+1}X_nT in which "n" corresponds to the number of layers and are typically 4 or lower. MXenes were first reported by Gogotsi and Barsom in 2011 by Al etching of the corresponding Ti₃AlC₂ precursors and subsequent exfoliation^[2] (Figure 1).

MXenes have expanded the family of known 2D nanomaterials in which the layers have only a few atoms thickness, adding new structures with high transition metal content in their composition.^[3] Among the many interesting physicochemical properties of MXenes, electrical conductivity has determined their immediate applicability as active components in electricity storage devices, such as in batteries and supercapacitors, and as electrocatalysts.^[4,5] In only a few years, MXenes have become among the most widely researched electrocatalysts for hydrogen evolution reaction,^[6] oxygen reduction reaction^[7] and electrocatalytic CO₂ reduction,^[8] among other electrochemical reactions.^[9]

MXenes are also receiving an increasing attention in photocatalysis, initially as alternative to the use of noble metal cocatalysts, generally in combination with organic dyes,^[10–14] but more recently exploiting the intrinsic semiconducting properties of some MXenes as photocatalysts.^[15–17] Figure 2 summarizes MXene properties and main applications.

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2. MXenes as Thermal Catalysts

In comparison to electro- and photocatalysis, the use of MXenes in thermal catalysis has almost been ignored up to now with only a handful number of studies in the literature, dealing with hydrogenation of CO₂ and furfural, dehydrogenation of ethylbenzene and formic acid, high temperature water gas shift, dry reforming and aromatization of CH₄ carried out at temperatures of 500 °C or higher.^[18] Figure 3 shows some of the reactions in which MXenes have been reported to act as thermal catalysts so far.

This situation sharply contrasts with the current state of catalysis that is dominated by the use of transition metals as active sites. Thus, it can be expected a considerable growth and expansion in the use of MXenes as solid catalysts in the near future. The present “*Concept*” article focuses on the potential that MXenes can offer in heterogeneous catalysts,^[19] providing new experimental results from our group to support the validity of some of the claims that will be proposed here.

Transition metals as active sites can promote reductions, oxidations, couplings and rearrangements, among other reaction types.^[20–22] While late transition metals are easier to reduce and they catalyze reactions in their metal state, early transition metals are considerably more oxophilic. For this reason, early transition metal catalysts are frequently metal oxides. In metal oxides, the most common groups present on the surface are M–O–M, M–O–H and M=O.^[23,24] Several of these surface groups with early transition metals have been reported to catalyze important chemical reactions, like the cases of Ti–OH,^[25] V=O,^[26] Nb=O,^[27] etc. This general comment is important regarding the possible use of MXenes in catalysis, since their composition is based on an early transition metal layer bonded to surface terminal groups that may have similarities with M–O–M, M–O–H and M=O on metal oxides.

3. Importance of the Surface Terminal Groups

The field of MXenes is led by theoretical studies that have shown how MXene properties, including electrical conductivity, adsorption energies and thermal and chemical stability are dominated by the nature of the surface termination.^[28] These predictions have been confirmed in numerous experimental studies showing the remarkable influence of surface terminal groups on the performance of MXenes in batteries, supercapacitors and electrocatalysis.^[29]

Further, surface termination is a key factor controlling the interlayer spacing of layered MXenes and, upon expansion, the material can exhibit, for example, a high ion intercalation capacity suitable for the development of high-capacity anode materials for non-lithium-ion batteries.^[30,31] On other hand, surface termination also influences metallic conductivity, surface defect density and other structural features that can be crucial in determining the activity of these MXenes in various fields, including electrocatalysis.^[32] It can be expected that these surface terminal groups can also be important in the possible use of MXenes as thermal catalysis.

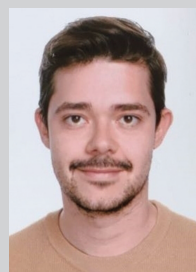
Surface terminal groups are generally installed on the MXene during the Al etching process, converting the M(Al)X precursor into the accordion-like phase. As HF, NH₄F/HCl and other fluorinating reagents in aqueous media are among the most widely used etching agents, common surface terminations in MXenes are –F, –O– and –OH groups bonded to the external M sheets of the MXene.^[33] These surface terminations can be



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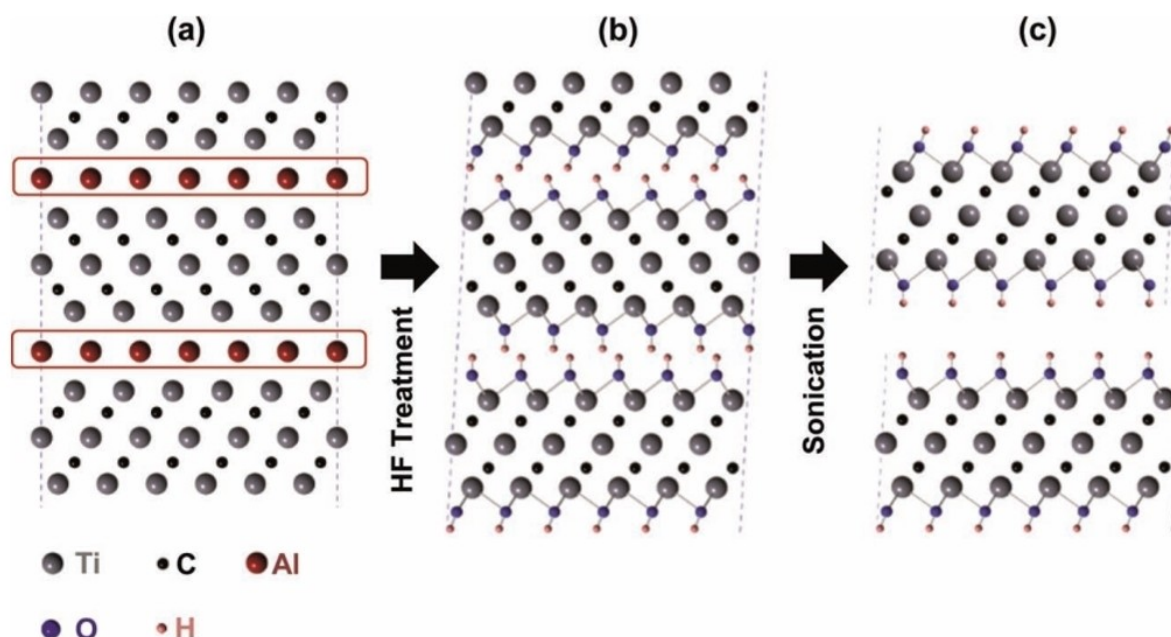


Figure 1. A general MXene synthesis procedure: a) Ti_2AlC_2 precursor. b) Al atoms replaced by OH groups after etching with HF. c) Breakage of the hydrogen bonds and separation of nanosheets upon sonication in methanol. Reproduced from ref. [2] Copyright (2011) with permission from Wiley-VCH.

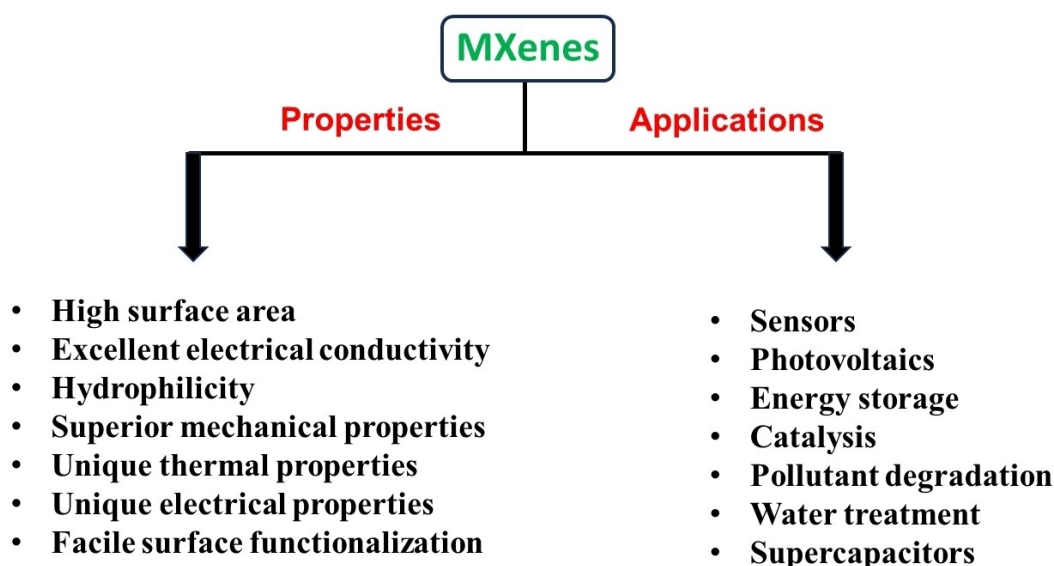


Figure 2. Some of the properties and applications of MXenes.

quantified by XPS analysis and by energy dispersive X-ray spectroscopy in the electron microscopy imaging of MXenes. The harsh corrosive conditions of F^- etching also determine the generation of structural defects in which no surface terminations or even an atom vacancy at the external M layer is generated.

However, since HF and other highly harmful F-containing reagents exhibit safety risks, there has been an interest in the field of MXene of developing alternative etching procedures,^[34] the use of Lewis acids^[34] in molten salt fluxes in the absence of water, being one general etching procedure that has been gaining increasing importance. Since the most common salts

used in the molten salt procedure are chlorides, then, the surface terminal groups in this etching procedure are chloride in *quasi* stoichiometric proportions. Surface defects can also be generated in molten salt etching due to the Lewis acid.

Even though additional more amenable methods for MAX etching are still much wanted and they will determine the possibility to install other surface terminations, it has been reported that, after the etching step, surface functional groups can be modified by post-synthetic treatments.^[35] Hydrogen annealing at high temperature can partially remove some oxygenated surface groups, fluoride forming the strongest bond being the most difficult to remove.^[35] Although under

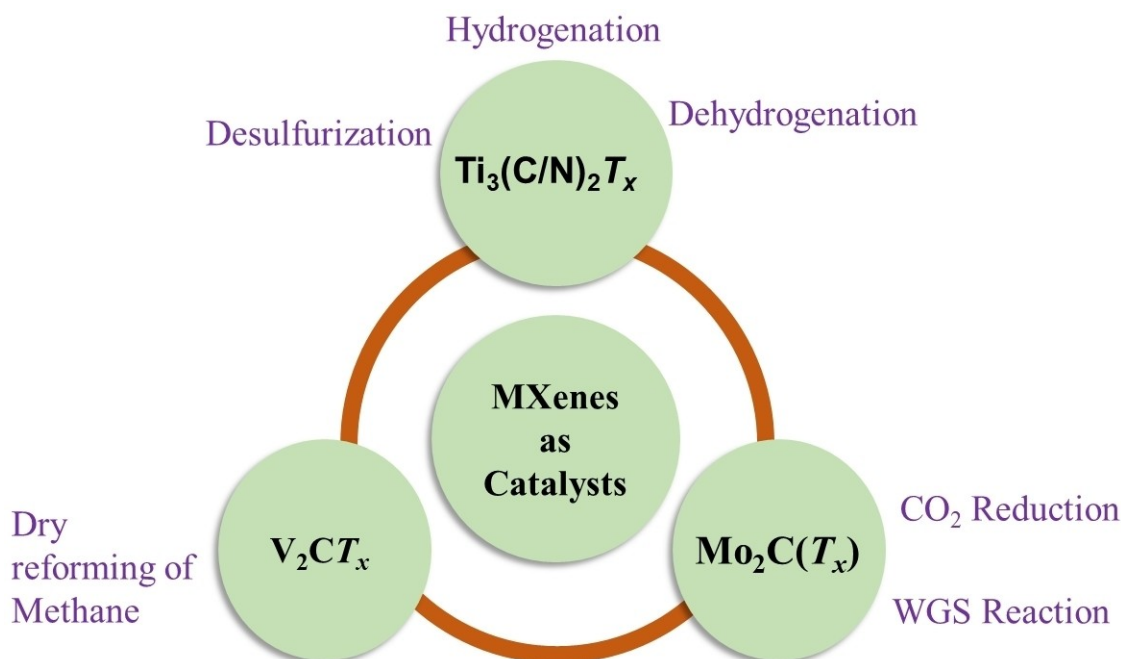


Figure 3. Some of the reported reactions using MXenes as catalysts. WGS stands for water-gas shift.

very different experimental conditions, there is also evidence showing that stirring aqueous suspensions of MXenes in the presence of strong oxidizing agents such as ammonium persulfate (APS) under controlled conditions increases the percentage of oxygenated surface terminations for MXenes samples obtained by etching with fluorinated agents.^[36] Prolonged treatment times with APS can result in a partial deterioration of the MXene structure.

In the case of surface-functionalized chloride MXenes, a general method to install other functional groups appears to be the treatment under molten salt conditions of the chlorinated MXene with a Li^+ salt of the anionic nucleophile that is going to replace Cl. The list of possible groups includes $LiNH_2$, $LiSe_2$ and LiX . The procedure also can be used starting with brominated MXenes.^[33] Figure 4 illustrates post-synthetic procedures that have been reported to change Br surface terminal group by $-O-$, chalcogenides and amide with a high level of exchange leading to well-defined MXene surface.

The probable relevance of the surface functional groups in catalysis comes from the consideration that, as commented, in the early transition metal oxide catalysts the active sites can be groups like $Ti-OH$, $Ti-NH_2$, $Ti-Cl$, $V=O$ and $Nb-OH$, among others, and that these groups can also be present in MXenes. Other possible defects of surface terminations can derive from their trend to generate vacancies exposing under coordinated transition metal centers and alteration of the electronic density and oxidation state of the metal atom bonded to them. Therefore, it can be anticipated that MXenes should exhibit some sort of catalytic activity. It can be argued that the Lewis acid character of these metal sites in metal oxides is different than those in MXenes due to their bonding with a carbide or nitride layer. It can be expected that the carbide or nitride

nature of MXenes will certainly play a role in their activity increasing the electronic density of the metal in comparison to similar sites anchored on oxide support. But, on one hand, MXenes could complement the array of transition metal catalysts by including materials whose metal electron density is higher than in oxides. On the other hand, it could be possible to further tune this electron density on the early transition metal by moving from carbides (higher electron density on the metal) to nitrides (lower electron density on the metal). Even more, it can be anticipated that the combination of various surface terminal groups can be used as additional tuning tool of the electron density at the metal site, through inductive effects exerted by electron withdrawing surface groups of the closest neighbors to the active site. In any case, the potential of MXenes to install in their surface functional groups similar to those that are considered active sites in metal oxides is evident and worth exploiting.

An obvious starting point to systematically explore the applicability of MXenes in thermal catalysis would be, therefore, to screen their activity as catalysts in those reactions that have been reported for the corresponding metal oxides or for metal complexes having similar coordination environment as in MXene.

Preliminary theoretical calculations should be used to give leading understanding on the feasibility of the catalytic activity in comparison to the metal oxide counterparts. These calculations should also propose modifications in the composition and surface terminations to further boost the catalytic activity of as-synthesized MXene samples. Activity tests on model reactions will provide initial exploratory information about the interest that MXenes as catalysts can present in this reaction. This first information can be subsequently used to develop

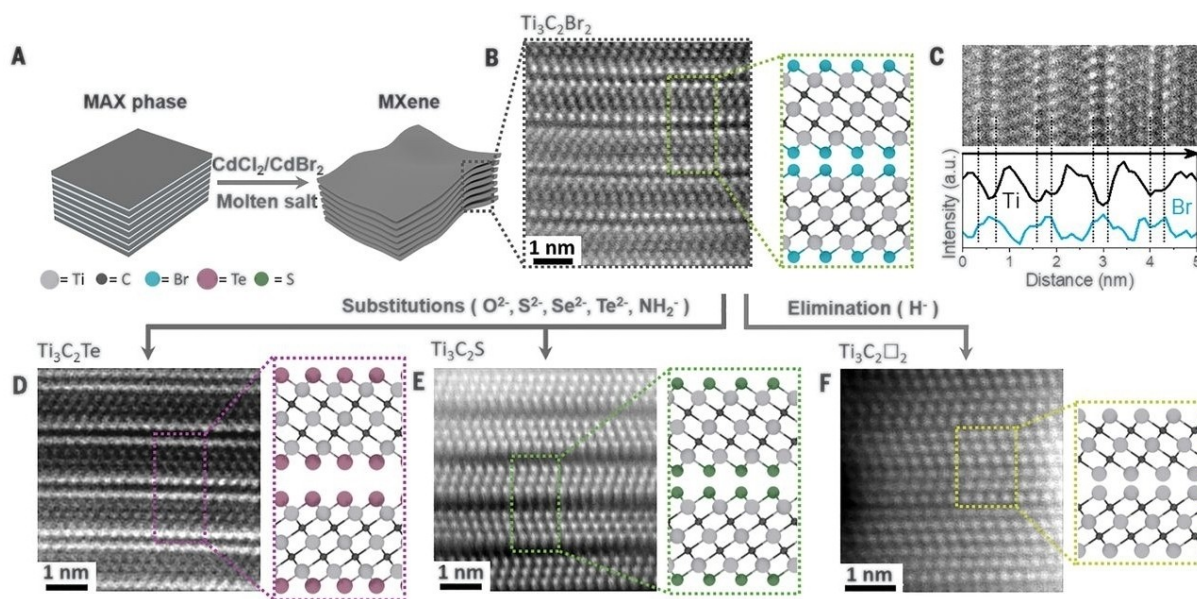


Figure 4. Surface reactions of MXenes in molten inorganic salts. (A) Schematics for etching of MAX phases in Lewis acidic molten salts. (B) Atomic-resolution high-angle annular dark-field (HAADF) image of $\text{Ti}_3\text{C}_2\text{Br}_2$ MXene sheets synthesized by etching Ti_3AlC_2 MAX phase in CdBr_2 molten salt. (C) Energy-dispersive X-ray elemental analysis (line scan) of $\text{Ti}_3\text{C}_2\text{Br}_2$ MXene sheets. HAADF images of (D) $\text{Ti}_3\text{C}_2\text{Te}$ and (E) $\text{Ti}_3\text{C}_2\text{S}$ MXenes obtained by substituting Br for Te and S surface groups, respectively. (F) HAADF image of $\text{Ti}_3\text{C}_2\text{□□}_2$ MXene (□ stands for the vacancy) obtained by reductive elimination of Br surface groups. Reproduced with ref. [33] Copyright (2020) with permission from American Association for the Advancement of Science.

more advanced catalysts based on specifically designed MXene samples.

The previous proposal to explore the potential that MXenes may have in thermal catalysis is going to be further presented using the previously unreported catalytic activity of V_2C to promote aerobic oxidation of benzylic hydrocarbons that is going to be described below.

4. V_2C as Aerobic Oxidation Catalyst

Vanadyl groups ($\text{V}=\text{O}$) have been anchored on silicas and other high surface area metal oxides to prepare active catalysts for aerobic oxidations.^[25] One of the major drawbacks of these $\text{V}=\text{O}$ anchored over metal oxides is their tendency to undergo leaching, phase separation and agglomeration as vanadium oxide. These restructurations lead to catalyst deactivation. It would be convenient to have a material in which $\text{V}=\text{O}$ are installed on the surface as a structural constituent of the material and, therefore, having the tendency to remain stable without leaching or segregation. This is in fact the case of V_2C MXene prepared by HF etching. Thus, to exemplify the potential of MXenes as catalysts, we are going to present the catalytic activity of V_2C in the aerobic oxidation of indane.

The V_2C sample used in the present study was obtained by Al etching of V_2AlC precursor using NaF/HCl mixture as etching agents.^[37] It is reported that this procedure leads to the accordion-like phase of unexfoliated V_2C in where the surface terminations are $-\text{F}$ and oxygenated groups, mainly, $-\text{O}-$ and $-\text{O}-\text{H}$.^[37] It is the hypothesis of the present *concept* that these $-\text{O}-$ or $-\text{O}-\text{H}$ groups should behave like analogous groups in

vanadium supported on metal oxides. It is clear, however, that the carbide nature of V_2C will determine an electronic density on V atoms that should be different than that of the $\text{V}=\text{O}$ groups anchored on silica and this should allow a certain degree of tunability on the catalytic activity of $\text{V}=\text{O}$.

To determine etching, XRD patterns of V_2C MXene with its MAX precursor is typically the most convincing evidence since it refers to the entirety of the material. In this sense, Figure 5 shows the effective etching of MAX precursor to afford V_2C solid by XRD patterns. Further, AFM image of the as-prepared V_2C MXene shows the average thickness of 4.15 nm as shown in Figure 6. Furthermore, TEM images of the V_2C solid also confirm the lamellar structure (Figure 7).

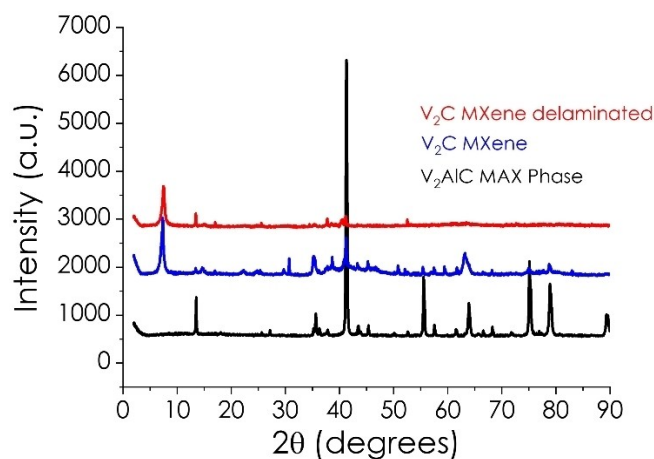


Figure 5. Comparison of the powder XRD patterns of MAX phase (black) and V_2C MXene in its accordion-like (blue) or delaminated (red) forms.

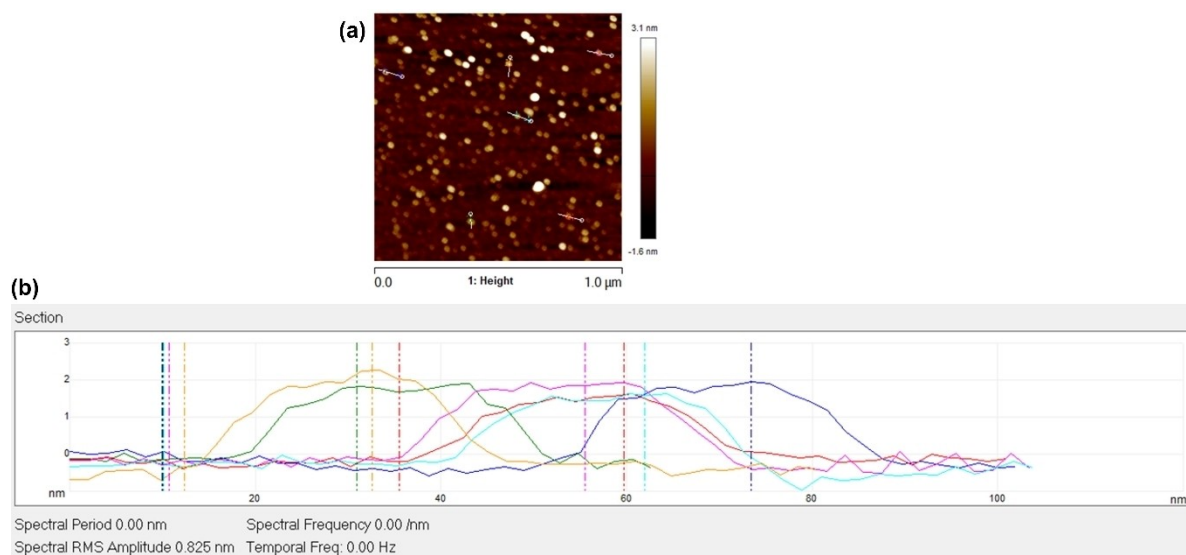


Figure 6. (a) Frontal AFM image of V_2C MXene and (b) shows the vertical profile corresponding to the thickness of the particles along the lines indicated in “(a)” with identical color.

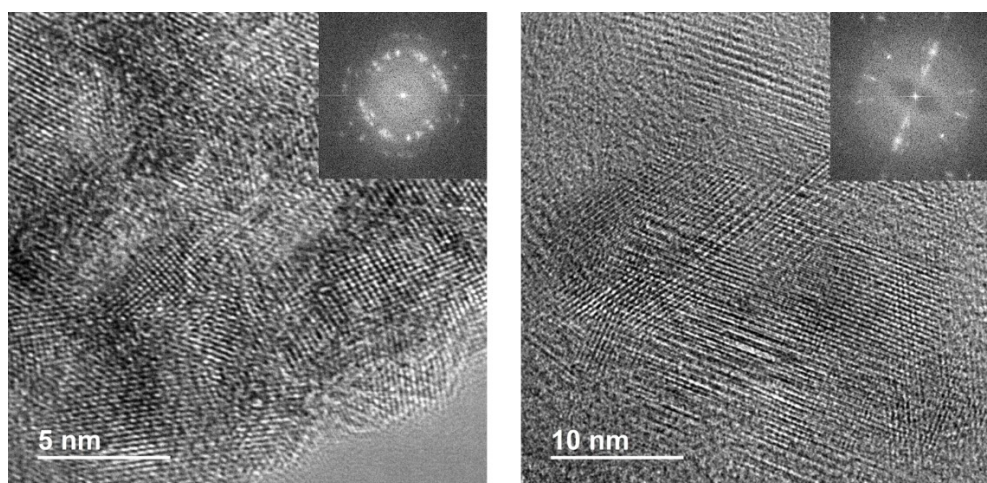
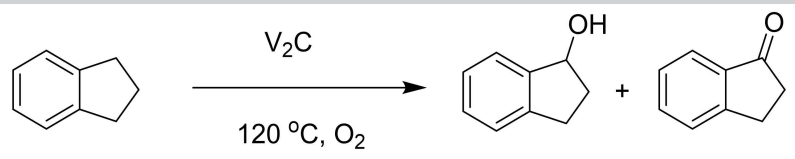


Figure 7. High resolution TEM images of the V_2C MXene used in the present study. The insets correspond to the selected area electron diffraction patterns of the sample showing its crystallinity.

To check the catalytic activity of V_2C , the aerobic oxidation of indane to a mixture of the corresponding indanol (ol)/indanone (one) was selected as a probe reaction, since there are abundant data in the literature about the reactivity of this substrate.^[38,39] In fact, we were pleased to observe that, under solvent-less conditions, heating at 120 °C, the accordion-phase of V_2C was able to promote this oxidation with a very high selectivity towards the ol/one mixture (Table 1, entry 5). The corresponding oxidation proceeds in very low conversion under N_2 , the residual minor oxidation being probably due to the imperfect removal of oxygen in the reaction system (Table 1, entry 3). While a control experiment in the absence of V_2C catalyst showed around 7% conversion of indane due to autooxidation (Table 1, entry 12). When the reaction is carried out at temperatures of 80 or 100 °C, no indane conversion was observed (Table 1, entries 1 and 2), meaning that oxygen and

heating at temperatures above 100 °C are necessary to promote indane oxidation.

It is known that BET surface area of accordion like MXenes is very low typically below 10 m^2/g . However, surface area can be notably increased upon exfoliation of the material. We have determined that Ti_3C_2 in suspension can exhibit a surface area over 100 m^2/g when properly exfoliated by using methylene blue association as a probe for surface area measurement. In the case of Ti_3C_2 , it was found that the photocatalytic activity increases with the degree of exfoliation. It is very likely that a similar increase in catalytic activity could occur upon V_2C exfoliation. In fact, it was observed that the catalytic activity of the accordion-like V_2C increases upon exfoliation that results in delamination of the MXene sheets, going from 18% indane conversion at 24 h reaction time to 41% at the same time under identical conditions (Table 1, entry 5). This is the result of

Table 1. Aerobic oxidation of indane using V₂C as catalyst under various experimental conditions.^[a]


S. No	Catalyst	Oxidant	T (°C)	Conversion (%) ^[b]	Selectivity of + one (%) ^[b]
1	V ₂ C	O ₂	80	–	–
2	V ₂ C	O ₂	100	–	–
3	V ₂ C	N ₂	120	2	–
4	V ₂ C bulk	O ₂	120	18	94
5	V ₂ C exfoliated	O ₂	120	41	95
6	V ₂ C exfoliated ^[c]	O ₂	120	89	88
7	V ₂ C exfoliated Run 2	O ₂	120	38	96
8	V ₂ C exfoliated Run 3	O ₂	120	35	93
9	V ₂ C exfoliated + <i>p</i> -BQ	O ₂	120	18	94
10	V ₂ C reduced with H ₂	O ₂	120	21	96
11	V ₂ C treated with APS	O ₂	120	24	95
12	No catalyst	O ₂	120	7	93

^[a] Reaction conditions: Indane (20 mmol), catalyst (10 mg), O₂/N₂ atmosphere through balloon, 24 h. ^[b] Determined by GC, products being confirmed by comparison with authentic samples. ^[c] After 72 h.

the increase in the surface area of the V₂C catalyst upon proper sheet separation.^[14] Similar studies comparing the catalytic activity of V₂C with other vanadium catalysts for the oxidation of other benzylic hydrocarbons under the same conditions have to be carried out to properly rank the activity of V₂C respect to other V catalysts particularly supported vanadyl materials.^[40]

The catalytic stability of exfoliated V₂C was tested in a series of three consecutive runs in which the same sample was used as catalyst after recovering it at the end of the reaction by filtration, washing the solid with acetonitrile and drying at reduced pressure. The results in Table 1 (entries 5, 7 and 8) show a constant selectivity with only a slight activity decrease that could really correspond to the incomplete catalyst recovery from run to run rather than to a real deactivation of the sample. Additionally, the long-term stability was checked by conducting aerobic oxidation of indane for 72 h and reaching a conversion of 89% (see entry 6, Table 1). This conversion is higher than the value measured at 24 h, thus supporting that the catalyst is still active, even in the presence of a large percentage of reaction products that could act as poisons.

However, characterization of the V₂C sample after reuses by TEM showed that although the 2D morphology (Figure 8) has been maintained, the V₂C sample after its extensive use as catalyst has undergone a significant degree of amorphization. Furthermore, EDS analysis for the reused V₂C sample indicates a loss of carbide in the composition. These data point towards a gradual loss of the MXene structure. In fact, stability is a general issue in heterogeneous catalysis that needs to be carefully addressed in every case. In the case of MXenes, it is known that stability increases with the number of layers and depends on the surface termination.

To determine the primary reactive oxygen species involved in the aerobic oxidation, *p*-benzoquinone (*p*-BQ, entry 9, Table 1) was used as selective superoxide radical quencher. The reaction was started under the general experimental procedure and then, at 4 h reaction time in which reactive oxygen species should have been build-up to a stationary distribution, *p*-BQ (20 mol% respect to indane) was added. It was observed that the presence of *p*-BQ decreases considerably the extent of aerobic oxidation, meaning that superoxide radical is involved in the reaction. In addition, filtration of V₂C in hot at 4 h of reaction time and subsequently continuing the oxidation under the reaction conditions, but in the absence of any solid catalyst, showed that the reaction stops. This indicates that the oxidation requires the presence of V₂C active sites to progress and that V₂C is acting as a real catalyst, rather than as a radical initiator of a long radical chain mechanism. This means that the chain length of the oxidation mechanism is small and that V₂C should not be considered an initiator of a radical chain mechanism, but as a catalyst with the active sites reaching a highest turnover number per V atom of 80 in the run corresponding to entry 5 of Table 1.

5. Modification of the Surface Termination Groups and Nature of Active Sites

When prepared by NaF/HCl etching of V₂AlC, the surface functional groups on V₂C are F, accompanied by –OH and –O– groups introduced by the aqueous phase.^[41,42] As commented above, it is well known that due to the radicaloid nature of the

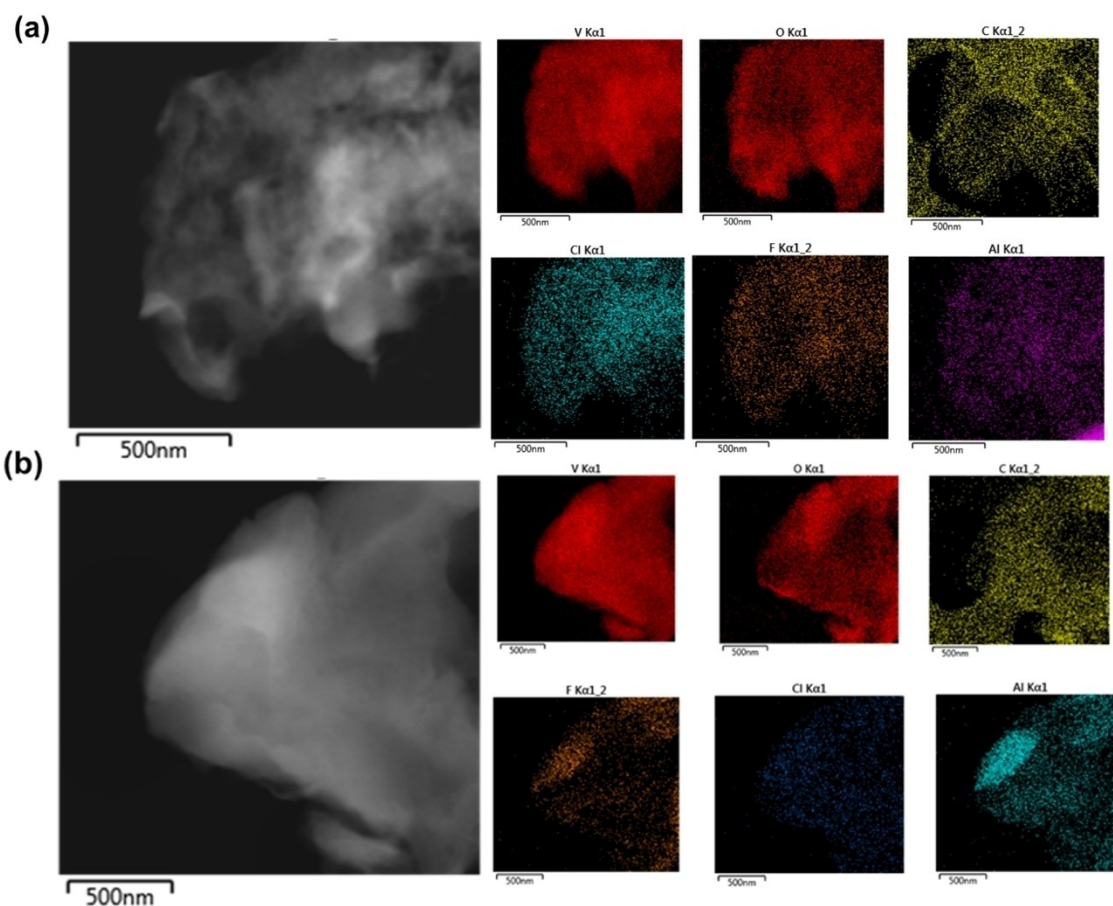
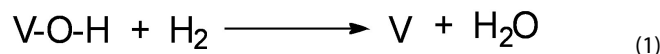


Figure 8. TEM and EDS images of the (a) fresh and (b) reused V_2C samples.

$V=O$ bond, this group anchored on the surface of metal oxides can be a center promoting hydrocarbon oxidations.^[43–46] It is reasonable to assume that similarly the oxygenated groups on the V_2C surface are responsible for promoting the aerobic oxidation in the case of V_2C . Note that the turnover number value requires that on average each V atom in the catalyst should promote the formation of 80 ol/one molecules and, therefore the sites are acting as catalysts, as shown by the lack of conversion when the solid catalyst is removed in the hot filtration test. However, it can be speculated that not all the V atoms are equally active in the reaction and that V–F sites are inert in the oxidation. Therefore, it should be possible to alter the catalytic performance of the original V_2C by submitting the sample to post-synthetic treatments that varies the surface composition.

In this regard, it has been reported that hydrogen annealing is a procedure to decrease surface hydroxyl terminations without altering crystallinity and structure of the MXene, according to eq. 1.^[47] Then, if V–O–H functional groups are somehow involved in the process, it could be expected that the catalytic activity would decrease by this treatment. In fact, after treating V_2C at 200 °C under a 50% H_2/Ar stream, the resulting H_2 -treated V_2C sample exhibited a notable decrease of about 50% in the catalytic activity (Table 1, entry 10).



Another frequently used procedure to modify the surface terminal groups is APS oxidation. While prolonged treatments with APS for hours can damage MXene structure, producing amorphization and appearance of metal oxides, reaction of APS with MXenes for less than 1 h has been reported to introduce surface –O– groups without altering crystallinity and structure of the MXene.^[48,49] Considering that V–O–H and V–O–V would behave differently as active sites, it was of interest to determine the influence of 30 min treatment of V_2C with APS. Besides surface –O– functional groups being favored, it can also be envisioned that the $V^{III/IV/V}$ oxidation state distribution can also be modified towards higher valent V. The results of APS treatment of V_2C are also included in Table 1 (entry 11) and, again, diminishes the catalytic activity of the original V_2C sample for the aerobic oxidation of indane at 120 °C.

To support the claims on the influence of the H_2 or APS treatment varying the distribution of the surface terminal groups, XPS analysis comparing the original V_2C sample with those resulting after the treatment was performed. High resolution XPS measurements were performed in the range of 510–540 eV zone corresponding the emitted electrons from O1s and V2p core levels as well as the C1s peak for the delaminated V_2C (Figure 9). The high resolution XPS between 510–540 eV

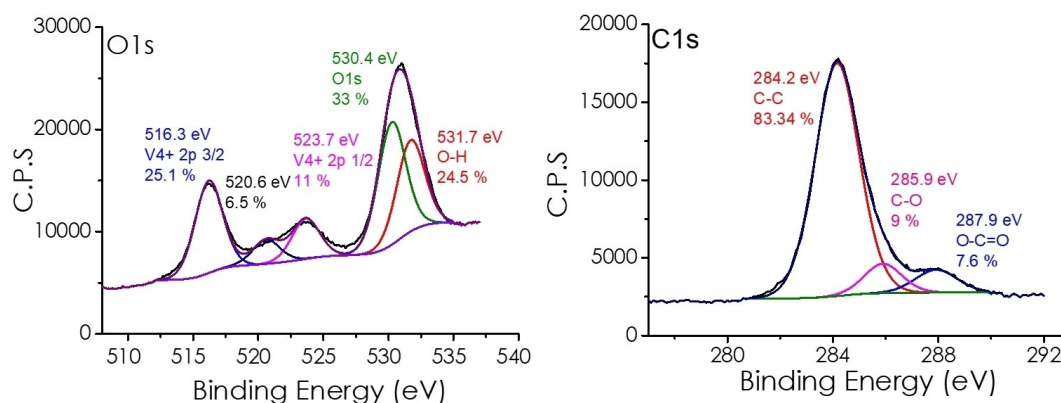


Figure 9. High resolution XPS peaks corresponding to the O1s and V2p (left) and C1s (right) core levels recorded for the V₂C sample before to surface treatment. The plots show the best deconvolution of the experimental peaks to the various components indicating their binding energy, the assignment and their percentage.

region for the treated V₂C samples is similar with changes in the proportion of the various components. Table 2 provides the atomic O/V ratio showing that H₂ and APS treatment decreases and increases O/V ratio, respectively. Furthermore, deconvolution of the O1s peaks for the original and treated samples shows that H₂ annealing decreases both –O–H and –O– surface groups, while APS favors significantly the –O– vs. –O–H group.

With these data at hand, it can be proposed that V^{III/IV}–OH groups, or defects derived therefrom, are the most likely active sites promoting aerobic oxidation. This proposal is based on the fact that H₂ treatment decreasing oxygenated functional groups decreases the catalytic activity, but also APS that increases the relative population of V–O–V at expense of V–O–H, also decreases the catalytic activity of the initial V₂C MXene.

6. Conclusions

The present *concept* article draws the attention of MXenes as promising heterogeneous catalysts in general organic transformations. Inspiration comes from the consideration of the presence of oxygenated M–OH and M–O–M surface groups in these 2D nanomaterials and realization that these groups are active sites in a variety of reactions. Based on this leading concept, a case has been selected, namely V₂C obtained by fluoride etching from V₂AlCl precursor and found that it has catalytic activity in the aerobic oxidation of indane as probe molecule. It has been proved that this catalytic activity

decreases when the surface functional groups are modified by chemical treatment decreasing the population of V–O–H groups. Understanding of the active site structure could lead to prepare on-purpose designed MXenes especially suited as catalysts with enhanced concentration of active sites. At long-term research on the catalytic activity of MXenes can provide a clear view on the advantages and opportunities that these noble materials offer in comparison with metal oxides. While the catalytic activity of metal oxides has been studied over many decades and there is a considerable wealth of information on their preparation, activity and stability, much research is needed in MXenes to reach a comparable degree of maturity. However, on the other hand, MXenes could cover some opportunities on catalysis that have not been achieved with metal oxides, particularly regarding control of the product selectivity. Special attention should be paid to delineate the reaction conditions in which MXenes are unstable and undergo decomposition.

Experimental Section

Preparation of V₂C MXene

The V₂C MXene sample was synthesized by hydrothermal method using a 100 ml autoclave. 2 g of V₂AlCl were added into a solution of 2.1 g NaF and 40 ml HCl previously prepared and the suspension stirred for 15 min. Then, the mixture was kept in autoclave at 90 °C for 5 days. After this time, the solid was collected by centrifugation and washed with Milli-Q water until the washing waters reached pH near 7.

After Al etching, delamination of the accordion-like V₂C MXene was carried out by 5 h ultrasonication with a ultrasound tip (500 W) using DMSO as dispersing agent. Afterwards, the material was filtered, washed with ethanol and the resulting V₂C solid dried at 70 °C in a vacuum system overnight.

Surface Functional Group Modification

V₂C treated under H₂ was prepared by treating 15 mg of delaminated V₂C with Ar/H₂ mixture (50/50) gas flow at 200 °C for

Table 2. Surface O/V atomic ratio and deconvolution of the O1s peak into the –O– and –O–H components.

Sample	O/V atomic ratio	Relative atomic proportion	
		–O–H	–O–
Initial V ₂ C	1.32	24	33
V ₂ C after H ₂ treatment	0.92	17	30
V ₂ C after APS treatment	1.70	22	41

1 h. After cooling the reactor, the reduced solid was used for catalytic reaction. Similarly, 20 mg of V_2C were dispersed in a solution of 20 mg of APS dissolved in 5 mL of water. This suspension was stirred at room temperature for 1 h and then, filtered. The recovered solid was dried at 150 °C for 4 h. This dried solid was used for catalytic experiment.

Reaction Procedure

In a typical catalytic experiment, a round bottom flask (25 mL) was charged with catalyst (10 mg) followed by addition of 20 mmol of indane. This slurry was connected to oxygen balloon to maintain a continuous bubbling through the system. Then, this suspension was heated under magnetic stirring at the required temperature (typically 120 °C) during the reaction time. Aliquots were sampled at different time intervals to monitor the progress of the reaction. An aliquot with a known volume was diluted to a known volume of acetonitrile containing a known amount of nitrobenzene as external standard. Analysis of the reaction mixture was performed using gas chromatography (Agilent) employing helium as carrier gas and a flame ionization detector. The reaction products were confirmed by GC-MS (Agilent) as well as by co-injection with authentic samples.

A similar procedure was followed for the quenching experiment in the presence of *p*-BQ by adding 20 mol% of this compound at 5 h. Hot filtration test was also performed by starting the reaction under the general procedure. After the initiation of the reaction, the solid catalyst was removed after 5 h by filtration through 5 mL syringe filter and the resultant solution without solid catalyst is allowed further to react under aerobic conditions. The analysis of the products was performed as described earlier.

Instrumentation

X-ray photoelectron spectra (XPS) were recorded using a spectrometer equipped with a MCD-9 detector under ultrahigh vacuum (1.3×10^{-13} atm) exciting with a monochromatic X-ray source. The binding energy values were calibrated against graphitic C1s as reference. XPS peaks were analyzed using the CasaXPS processing software. Powder XRD was carried out using a Philips XPert diffractometer with Ni filtered Cu $K\alpha$ radiation. TEM images were captured with a field emission TEM (JEOL JEM-2100F instrument) operating at 200 kW.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords: Aerobic oxidation · Indane · Mxene · Thermal catalysis · Vanadium carbide

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