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Ti₃AlC₂ MAX-phase as an efficient catalyst for oxidative dehydrogenation of n-butane

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Abstract: Light alkenes are important raw materials for the synthesis of polymers and other chemical products. Traditionally they are obtained mainly from steam cracking and catalytic cracking units. However, dehydrogenation or oxidative dehydrogenation (ODH) of alkanes is gaining more importance to produce alkenes directly from natural gas/shale gas. Here we report that Ti₃AlC₂, a MAX phase, which hitherto had not used in catalysis, efficiently catalyses the ODH of n-butane to butenes and butadiene, important intermediates for the synthesis of polymers and other compounds. The catalyst, which combines both metallic and ceramic properties, is stable for at least 30 h on stream, even at low O₂:butane ratios without suffering from coking. This material has neither lattice oxygens nor noble metals, yet a unique combination of numerous defects and a thin surface Ti_{1-x}Al_yO_{2-y/2} layer that is rich in oxygen vacancies makes it an active catalyst. Given the large number of compositions available, MAX phases may find applications in several heterogeneously catalysed reactions.

MAX phases, a term coined in the late 1990s, are a family of ternary carbides and nitrides with layered hexagonal crystal structures. Their name reflects their chemical formula: M_{n+1}AX_n—where M is an early transition metal, A is an A-group element (mostly groups 13 and 14), X is carbon and/or nitrogen, and n = 1, 2, or 3 (see Figure 1). Most of these phases were discovered in powder form already in the 1960s, though the synthesis of phase-pure bulk samples was only achieved in 1996.^[1] MAX phases are interesting because they exhibit a unique combination of ceramic and metallic properties.^[2-4] Their bonding is a combination of covalent and metallic.^[5] The density of states at the Fermi level is substantial and dominated by the d-d orbitals of the M-element.^[5] The electrical resistivity is metal-like in that it

drops linearly with decreasing temperatures. They conduct heat and electricity like metals, yet they are elastically stiff, strong, brittle, and some are heat-tolerant like ceramics.^[6]

Numerous studies have been published on the electrical, thermal and mechanical properties of MAX phases.^[7-12] However, to the best of our knowledge, no catalytic applications have been reported so far. Considering the combination of metallic and ceramic properties and high stability, we anticipated that these materials could be good catalysts. Moreover, the fact that they differ from most “conventional” catalytic materials (because they are neither oxides nor pure metals) triggered our curiosity. Such different materials may open reaction pathways that are unavailable to traditional catalysts.

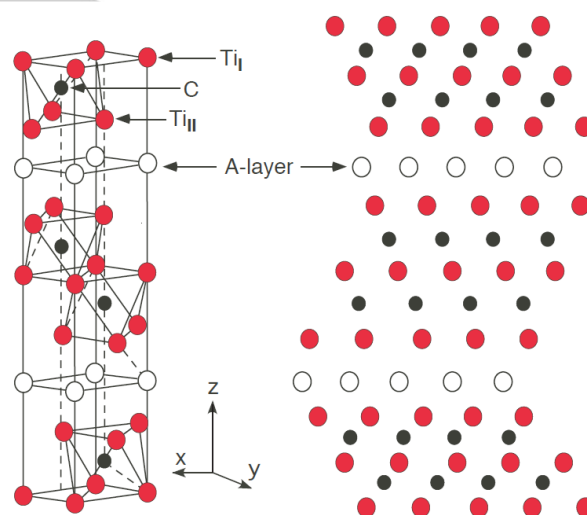


Figure 1. Hexagonal crystal structure of a 312 MAX phase. Ti atoms have two different sites, denoted Ti_I and Ti_{II}. Every fourth layer is interleaved with layers of pure A-group element.

Considering the layered structure with alternating metals and non-metals and thermal stability, we opted to study the catalytic application of MAX phases in oxidative dehydrogenation (ODH).^[13-18] Specifically, we examined the oxidative dehydrogenation of butane to butenes and 1,3-butadiene (Scheme 1). Butenes, and especially butadiene are important industrial precursors for producing synthetic rubbers and plastics. This reaction has recently gained importance with the advent of shale gas and the increased use of natural gas as a cleaner carbon source.^[15, 19-29] The problem is that the typical conditions

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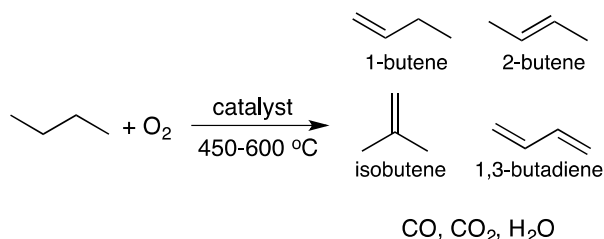
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Supporting information (full experimental details, PALS, TEM, XPS, EDX results, modelling procedures and results) for this article is given via a link at the end of the document.

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that can activate alkanes often lead to low alkene selectivity, because the products oxidise further to CO and CO₂. We now report the discovery that Ti₃AlC₂, a commercially available MAX phase, is a highly active and selective catalyst for butane ODH. It gives high yields of C4 alkenes, especially 1,3-butadiene.



Scheme 1. The catalytic oxidative dehydrogenation of butane can give butenes, butadiene, CO and CO₂.

We synthesized the Ti₃AlC₂ MAX phase by a ceramic synthesis route and confirmed its structure by X-ray diffraction (see Supporting Information for full experimental details). It consists of a c-axis stacking sequence where two layers of edge sharing CTi₆ octahedra are sandwiched between planar layers of Al. The butane ODH study with Ti₃AlC₂ was carried out at different temperatures, varying the O₂:butane ratio from 0.25:1 up to 1:1. The product mixture contained 1-butene, 2-butene, butadiene, propene, CO₂ and CO. Control experiments without a catalyst yielded <1% of alkenes. At an O₂:butane ratio of 0.25:1 and 550 °C, Ti₃AlC₂ gave nearly 35% selectivity for butenes and 25% selectivity for butadiene at 10% conversion (Table 1). At higher O₂/butane ratios of 0.5 and 1, conversion increased to 20% and 24%, respectively, without significant loss in selectivity for butenes and butadiene. Even at 24% conversion, the partial oxidation (butenes+butadiene) selectivity is close to 50%, which is remarkable. The catalyst was stable, retaining its selectivity during a long-time test (Figure S1). XRD analysis after the reaction did not show any major structural changes further confirming the stability of the phase (Figure S2).

Table 1. Performance of the Ti₃AlC₂ in butane ODH

O ₂ :butane molar ratio ^[a]	Butane conversion, %	Total selectivity of butenes, %	Selectivity of 1,3-BD %	Selectivity of propene % ^[b]
0.25:1	10.1	35.0	25.0	1.2
0.5:1	20.3	29.0	21.0	1.4
1:1	24.2	27.0	19.5	1.7
1:1 [#]	13.8	20.7	16	1.6

^[a]Reaction conditions: temperature = 550 °C; flow rate = 17 mL/min; catalyst = 0.1 g; total pressure = 1 bar. ^[b] trace amounts of ethylene and methane were also produced. The remainder is CO and CO₂. [#]Temperature = 500 °C.

Such high selectivity for butadiene is rarely achieved in butane ODH. At the same conversion of butane, Ti₃AlC₂ was more selective for butenes and butadiene than Mg₃V₂O₈ or Mg₃V₂O₇, that are amongst the best catalysts reported so far for this reaction.^[29] Remarkably our Ti₃AlC₂ catalyst was still active and stable at O₂:butane ratios ≤ 1:1 (see Table 1 and Figure S1). Typical metal oxide catalysts require ratios ≥ 2:1 to prevent severe deactivation due to coke deposition.^[29]

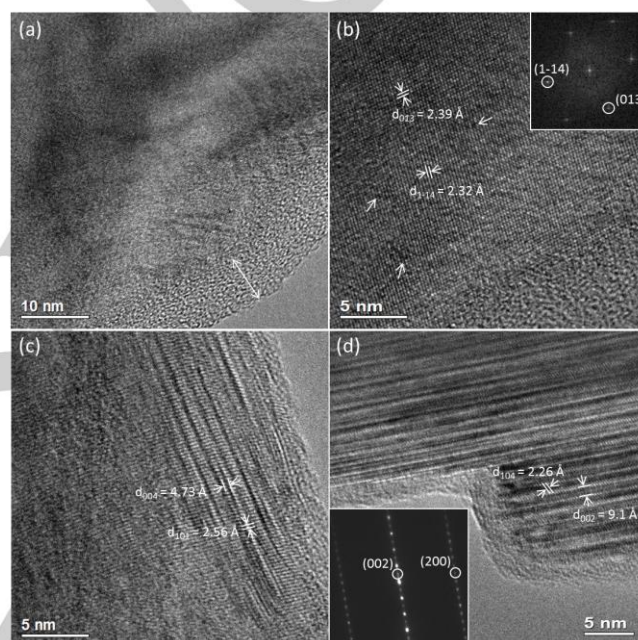


Figure 2. HRTEM images of Ti₃AlC₂ MAX phase. (a) A thin pale contrasted amorphous surface layer (marked by arrow). (b) Higher magnification HRTEM image of a selected area in (a) showing many point defects (marked by arrows). (c) HRTEM image showing many disordered layer defects. (d) HRTEM image showing many partially ordered layer defects. The inset shows the corresponding SAED pattern. The marked d-spacings are indexed to the unit cell of Ti₃AlC₂.

The initial steps of the ODH reaction (O₂ and alkane activation), normally follow a Mars–Van Krevelen mechanism for metal oxides, wherein the lattice oxygen is the reactive species. This means that the activity of metal oxide catalysts towards hydrocarbons depends on the strength of the metal–oxygen bond of the catalyst. In our case, there are no bulk lattice oxygens available, making the adsorption of oxygen on the catalyst surface to generate active oxygen species inevitable for the reaction to occur. This adsorption depends strongly on the defect sites at the catalyst surface. The HRTEM analysis indeed showed that the catalyst particles contain many defects, most commonly domain, point and layered ones (Figure 2). These defects might act as adsorption as well as reaction sites. Positron Annihilation Lifetime

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Spectroscopic investigation (PALS) of our catalyst showed two positron lifetime components (see Table S1 and Figure S3), which are higher than the bulk positron lifetime in titanium carbide (107 ps) indicating positron annihilation from defect sites.^[30] The first lifetime component (189.7±6.1 ps) is very close to the positron lifetime for monovacancy of Ti indicating the existence of Ti vacancy defects. The second lifetime component (300.9±9 ps) is attributed to defects with larger open volume like vacancy clusters and voids. This agrees well with the HRTEM observation of layered defects. Positron trapping to these defects will lead to higher lifetime value. The corresponding intensities of the positron lifetime components indicate that concentration of mono vacancy defects are higher than the layer defects. HRTEM further shows a thin amorphous layer (5–10 nm) on the surface (Figure 2a), which according to EDX spectra contains a very high oxygen content compared to the inner bulk material (see Figure S4, Supporting Information). The X-ray from oxygen has very low energy and can be easily absorbed so the oxygen content in an EDX spectrum may not be accurate, therefore quantitative data analysis is not provided. Further confirmation of a high oxygen content in the amorphous surface layer was provided through EDX elemental mapping (Figure 3).

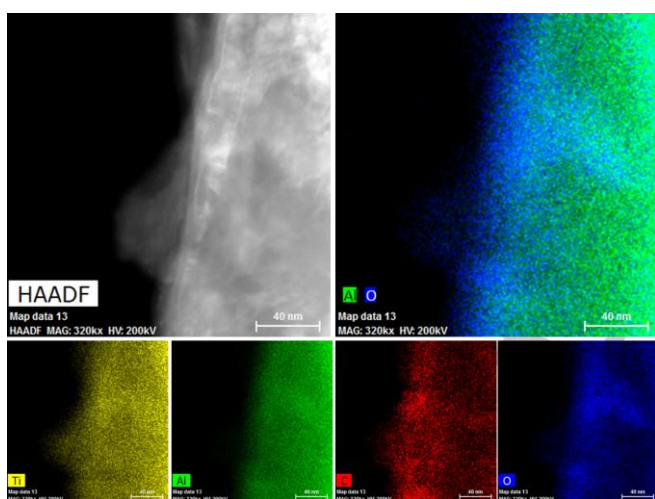


Figure 3. HAADF STEM image (top left) and elemental maps for Al + O (top right) and Ti, Al, C and O on the Ti_3AlC_2 MAX phase (bottom).

Based on the analysis of EDX spectra and mapping, we reason that the thin layer on the catalyst surface is a mixed oxide of Al-Ti-O. Alternatively, we considered it may be pure alumina or alumina/titania but this appears to be less likely according to our EDX mapping data. We believe that this thin layer, coupled with the large electron reservoir below it, holds the key to the catalytic activity.^[31] To confirm this, we studied the catalyst by XPS (see Figure 4), which has indeed proved that, besides the individual carbide peaks, the surface has a significant amount of mixed oxides as well as oxidized Al and Ti. This supports our hypothesis that the surface layer observed by TEM is a mixed Al-Ti-O. Alumina and titania can form a solid solution with the formula, $(\text{Ti}_{1-y}\text{Al}_y)\text{O}_{2-y/2}$,

creating a mole of oxygen vacancies for every two moles of alumina that is added. Previous studies indicated that, after high temperature oxidation, a $(\text{Ti}_{1-y}\text{Al}_y)\text{O}_{2-y/2}$ layer is formed on the surface of Ti_3AlC_2 .^[32–33] It is reasonable to assume that the oxygen vacancies should also act as active oxygen ‘creators’ from gas phase oxygen, which can explain the catalytic activity. The adsorbed oxygen species formed upon activation of gas-phase O_2 on surface oxygen vacancies can activate *n*-butane. These species are most likely monoatomic, and therefore more selective for partial oxidation.^[28]

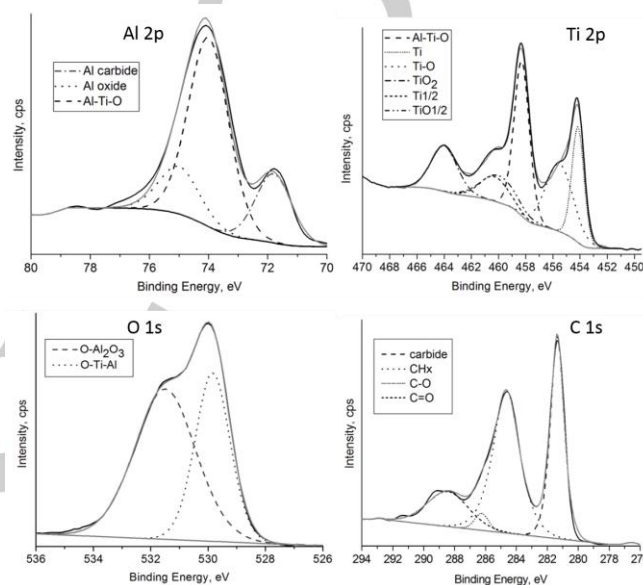


Figure 4. Al2p, Ti2p, O1s and C1s XPS of Ti_3AlC_2 , showing different types of possible species on the surface. Besides individual carbide and oxide, the surface has a significant amount of mixed oxide (Al-Ti-O).

We used N_2O chemisorption coupled with XPS analysis to estimate the concentration of oxygen vacancies using the fact that metallic sites will split adsorbed N_2O at required activation temperature, leading to the oxidation of metal to metal oxide.^[34] Thus, we first reduced the Ti_3AlC_2 MAX phase in UHV (10^{-7} mbar) at 500 °C, creating oxygen vacancies and subsequently exposed the reduced surface to N_2O . We then examined the re-oxidised surface by XPS. The amount of Ti that undergoes oxidation can be estimated by linear extrapolation of the subsurface (diffusion dependent oxidation) uptake to $t=0$ (see Figure S5),^[35] which gives 3.5 at%. The corresponding oxygen amount is 7.0 at%. Using this, we can estimate the concentration of oxygen vacancies as $9 \times 10^{26}/\text{m}^3$ (see Supporting information and Figure S6 for more details).

To further prove the role of oxygen vacancies, we also tested another MAX phase Ti_3SiC_2 , isostructural with Ti_3AlC_2 wherein the Al layers are replaced by Si.^[1, 36] The difference here is that unlike alumina and titania, silica and titania do not form a solid solution. Hence, if our hypothesis that the $(\text{Ti}_{1-y}\text{Al}_y)\text{O}_{2-y/2}$ layer is responsible for the catalysis, Ti_3SiC_2 should be much less selective in ODH. A series of control experiments at varying temperatures proved that

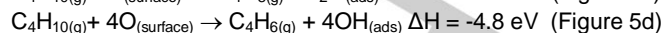
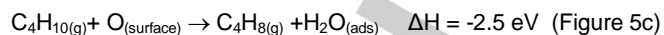
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to be true. Ti_3SiC_2 gave lower conversion (from 4 % at 450 °C up to 16 % at 600 °C compared to 24% at 550 °C for Ti_3AlC_2) and the total yield of butene and butadiene was only 1–2 % (Table S2, Supporting Information). This confirms that the lack of sufficient anion vacancies in Ti_3SiC_2 due to the inability to form a non-stoichiometric surface over layer leads to non-selective oxidation in this case. Kondratenko *et al.* recently reported enhanced selectivity for propene in non-oxidative dehydrogenation of propane by deliberately increasing the concentration of defect sites in unconventional oxide catalysts.^[37] They promoted ZrO_2 , which has an unchangeable oxidation state, with other metal oxides, which created lattice defects consisting of coordinatively unsaturated Zr cations. Our results further confirm that the defective structure in unconventional materials can generate unexpected catalytic properties. Moreover, stable activity and selectivity over several hours (Figure S1) indicate high surface mobility of oxygen anions and consequent rapid reoxidation apparently due to the layered structure of our Ti_3AlC_2 MAX phase. Since adsorption of butane on the surface also will influence the reaction, we also compared the relative adsorptions of n-butane on both samples at 250 °C (highest temperature possible in our adsorption equipment). These experiments showed that Ti_3AlC_2 adsorbs significantly more n-butane than Ti_3SiC_2 (Figure S7), apparently due to the defective structure.

To understand further the experimental observations, we evaluated computationally a number of scenarios of favourable chemical reactions at the surface. Note that this is not an exhaustive search. Since a previous equilibrium study has shown that a stable ternary phase of Al_2TiO_5 exists in the Ti-Al-O system,^[38–39] we used the O-terminating (001) surface of this phase as a simple model to represent the mixed-cation oxide surface on Ti_3AlC_2 MAX phase. We performed electronic structure calculations as implemented in the Density Functional Theory approximation (VASP *ab initio* code^[40]) to assess the energetics of the adsorption of butane onto the oxygen-terminating surface at the ground state (at 0 K). Further details of the methodology, exchange-correlation potentials used (PAW-PBE^[41]) and convergence criteria (electronic convergence criterion of 10^{-5} eV and force convergence limit of 10^{-2} eV/Å) are given elsewhere.^[42–43] Table S3 (Supporting Information) shows the list of chemical reactions along with the final atomic configurations.

The results show that butane adsorbs relatively easily, through the formation of a C–O bond on the selected surface. This is followed immediately by the dissociation of the hydrogen atom onto the surface, captured by one of the oxygen's dangling bonds: $\text{C}_4\text{H}_{10}(\text{g}) + \text{O}_{(\text{surface})} \rightarrow \text{C}_4\text{H}_9(\text{ads}) + \text{OH}_{(\text{ads})}$; $\Delta H = -2.99$ eV. Figure 5a shows the resulting atomic configuration (A video showing the relaxation sequence is included in the SI). This reaction releases roughly 3 eV per molecule of butane. A possible subsequent reaction where by the adsorbed C_4H_9 further decomposes into $\text{C}_4\text{H}_8(\text{ads})$ by releasing another hydrogen atom forming a water molecule (Figure 5b) is also favoured, for an overall chemical reaction of: $\text{C}_4\text{H}_{10}(\text{g}) + \text{O}_{(\text{surface})} \rightarrow \text{C}_4\text{H}_8(\text{ads}) + \text{H}_2\text{O}_{(\text{ads})}$; $\Delta H = -3.35$ eV. A further oxidative dehydrogenation may be facilitated by the release of more hydrogen atoms from the adsorbed C_4H_8 yielding 1,3 butadiene according to: $\text{C}_4\text{H}_8(\text{ads}) + \text{O}_{(\text{ads})} \rightarrow \text{C}_4\text{H}_6(\text{ads}) + \text{H}_2\text{O}_{(\text{ads})}$; $\Delta H = -1.39$ eV. Overall, releasing two or four hydrogen

atoms from butane onto the surface yielding adsorbed water molecule/forming OH bonds is favourable on the Al_2TiO_5 surface:



As shown in reaction # 2 in SI, the overall desorption reaction $\text{C}_4\text{H}_{10}(\text{g}) \rightarrow \text{C}_4\text{H}_9(\text{g}) + \text{H}_{(\text{ads})}$ is slightly endothermic, with $\Delta H = 0.9$ eV. This value however is much lower than the energy required for releasing the intermediate product of $\text{C}_4\text{H}_9(\text{ads})$ into $\text{C}_4\text{H}_9(\text{g})$ ($\Delta H = +3.89$ eV). Thus, both types of direct dissociation will not be the easiest pathways and thus, other intermediate mechanisms must have taken place to lower these overall energy barrier. This gives credence to the possible role of oxygen defects and/or a higher operating temperature to enable the reaction to proceed. Nevertheless, the overall reactions involving further dissociations do indicate energetically favourable conditions for oxidative dehydrogenation of butane on a mixed Al-Ti-O surface into butane and butadiene.

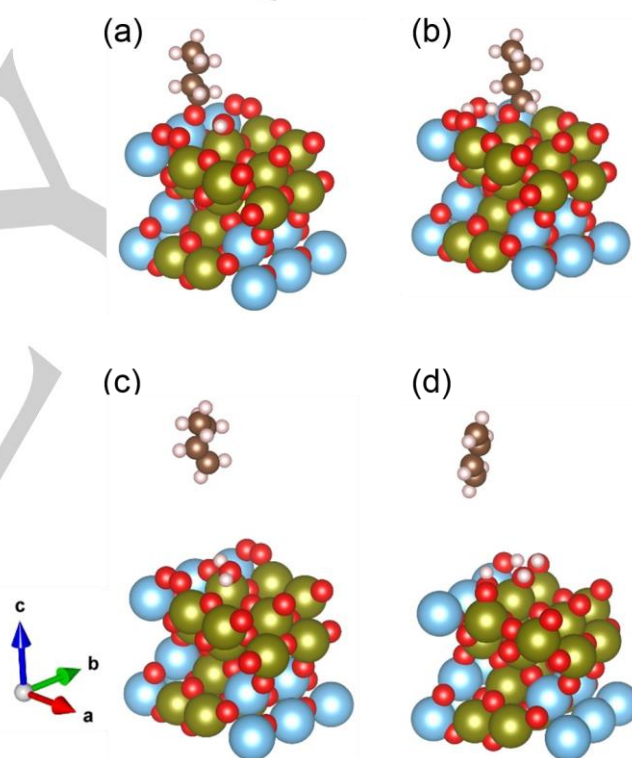


Figure 5. Atomic configurations of various steps of butane interaction with the MAX surface, taking Al_2TiO_5 as a model resulting in (a) $\text{C}_4\text{H}_9(\text{ads}) + \text{OH}_{(\text{ads})}$, (b) $\text{C}_4\text{H}_8(\text{ads}) + \text{H}_2\text{O}_{(\text{ads})}$, (c) $\text{C}_4\text{H}_8(\text{g}) + \text{H}_2\text{O}_{(\text{ads})}$ and (d) $\text{C}_4\text{H}_6(\text{g}) + 4\text{OH}_{(\text{ads})}$. See the Supporting Information for more details. Ti is represented by blue balls and O by red balls.

There is no lattice or structural oxygen in Ti_3AlC_2 MAX phase, and it doesn't contain any noble metals, yet its unique combination of defects and very thin presumably non-stoichiometric oxide surface layer containing oxygen vacancies resulted in O-containing active sites and made this material catalytically active. Given the interesting set of properties that the MAX phases exhibit,

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especially their high-temperature stability, metallic and ceramic properties and low cost, our work has very wide scope in heterogeneous catalysis. For an industrial process, we still need to resolve issues such as product separation and high recycle rate; however, we believe that our results will open new fundamental studies of MAX phases. There are over 60 MAX phases synthesized so far, with very different compositions. The unique properties of these materials as catalysts or catalyst supports in suitable reactions are waiting to be explored.

Acknowledgements

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Keywords: Butadiene • heterogeneous catalysis • natural gas • oxidative dehydrogenation • shale gas • VASP

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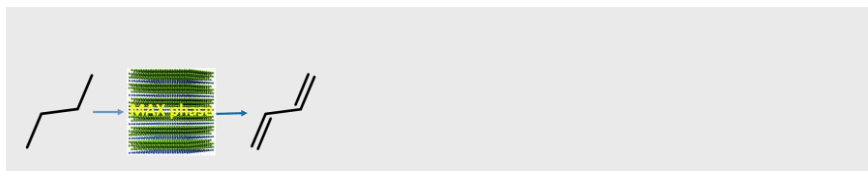
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Ti_3AlC_2 , the first MAX phase to be used in heterogeneous catalysis, efficiently catalyses the ODH of n-butane to butenes and butadiene, owing to its defective structure and non-stoichiometric oxide layer on the surface.

Wesley H. K. Ng, Edwin S. Gnanakumar, Erdni Batyrev, Sandeep K. Sharma, Pradeep K. Pujari, Heather F. Greer, Wuzong Zhou, Ridwan Sakidja, Gadi Rothenberg, Michel W. Barsoum* and N. Raveendran Shiju*

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Ti_3AlC_2 MAX-phase as an efficient catalyst for oxidative dehydrogenation of n-butane