- 1 Two-dimensional titanium carbide (MXene)-supported Pt3Ti intermetallic compound catalysts
- 2 for efficient room-temperature oxidative removal of gaseous formaldehyde
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20 Abstract

The present study explores the potential of reactive metal-support interactions between a two-21 dimensional titanium carbide (Ti₃C₂ [MXene]) support and platinum (Pt) to achieve 100% 22 formaldehyde (FA) conversion (X_{FA}) into carbon dioxide (CO₂) at room temperature (RT) in the 23 presence of air through the formation of a Pt₃Ti intermetallic compound. The RT steady-state reaction 24 rate (mol $g^{-1}h^{-1}$) of FA oxidation increased in the following order: 2% Pt/Ti₃C₂ (0.020) < 0.1% Pt/Ti₃C₂-25 26 R (0.054) < 1% Pt/Ti₃C₂-R (0.058) < 2% Pt/Ti₃C₂-R (0.061; turnover frequency of approximately 60 mmol_{FA} mol₀⁻¹ s⁻¹). The Pt₃Ti formed *in situ* during reduction pre-treatment (R) enhanced catalytic 27 activity, and 2% Pt/Ti₃C₂-R achieved significant resistance to moisture by maintaining 100% X_{FA} at a 28 relative humidity of 0%-90%. In situ diffuse reflectance infrared Fourier-transform spectroscopy 29 30 revealed dioxymethylene, formate, and carbon monoxide as the reaction intermediates of FA oxidation. Density functional theory simulations revealed that the carbonyl bond (C=O) of FA is activated by 31 chemisorbing on Pt₃Ti (the oxygen and carbon atoms in C=O adsorb on the Pt and titanium sites of 32 Pt₃Ti, respectively), generating CO₂ by reacting with active oxygen species, which form through the 33 decomposition of molecular oxygen on the Pt/Ti sites. Regarding the normalized reaction rate, 0.1 34 Pt/Ti₃C₂-R (0.55 mol g⁻¹ h⁻¹ [bulk Pt, wt.%]⁻¹) appears to be among the best-performing Pt catalysts 35 reported for FA oxidation at RT. 36

37	Keywords: Formaldehyde; MXene; Volatile organic compounds; Indoor air; Catalytic oxidation
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68 1. Introduction

Carbonyls such as formaldehyde (FA) are among the most widespread volatile organic compounds 69 (VOCs) in the air [1, 2]. Among the 187 hazardous air pollutants listed by the US Environmental 70 Protection Agency, FA has one of the highest estimated cancer risks [3]. In urban outdoor environments, 71 the primary anthropogenic sources of FA are on-site industrial and vehicular emissions, domestic 72 73 heating systems, and photochemical conversion of other VOCs in the atmosphere [4, 5]. In the indoor 74 air, FA is primarily produced and released from livelihood sources (e.g., wooden items and furniture containing FA-based resins, glues, paints, insulating materials, textiles, cosmetics, cleaning products, 75 electronic equipment, and other consumer goods) [1]. In light of the adverse health effects associated 76 with exposure to FA, the US Occupational Safety and Health Administration set the permissible 77 exposure limit at 0.75 ppm for an 8 h workday [6]. 78

Among the options available for mitigation of FA, catalytic total oxidation (e.g., conversion into 79 benign end products of water and carbon dioxide) under room temperature (RT) and dark conditions is 80 recognized as one of the most lucrative and practical [7-9]. The suitability of platinum (Pt) catalysts 81 for RT FA oxidation reactions has been studied extensively due to their superior activities and enhanced 82 deactivation resistance compared with other catalysts (e.g., transition-metal oxides) [10, 11]. However, 83 84 alkali-metal promoters such as sodium (Na) and potassium (K), are often needed to achieve complete FA mineralization into CO₂ at RT [12, 13]. Alkali metal-promoted Pt catalysts in FA oxidation 85 typically utilize metal oxides as synergistic supports to achieve a strong metal-support interaction 86 (SMSI) [13]. An SMSI enhances metal cluster stability and improved charge transfer to optimize 87 catalytic activity [13]. However, alkali-metal modification can reduce FA oxidation efficiency by 88 covering the catalytic sites unless the dispersion is controlled site-selectively [14], making fine-tuning 89 of the active Pt sites without the aid of an alkali-metal promoter necessary. 90

91 Recently, two-dimensional (2D) transition-metal carbides (MXenes in the form of $M_{n+1}X_nT_x$, in which M = early transition metal, X = nitrogen and/or carbon, and T = surface functionalities) have 92 been reported as active media for reactive metal-support interactions (RMSIs) [15-17]. Based on the 93 RMSI, supported metal catalysts can be tuned by reacting them with transition-metal ions from the 94 support and forming ordered intermetallic compounds (IMCs) [16, 18, 19]. The strength of the M-95 carbon bond in 2D MXenes is generally weaker than that of the M-oxygen bond in commonly utilized 96 97 oxide supports [16]. IMCs form readily at moderate temperatures via *in situ* reduction of MXenes due to the latter's enhanced reactivity [15]. Such formations are not possible for traditional carbide and/or 98 oxide supports [15, 16]. The strong bonds in IMCs (e.g., Pt₃Ti in Pt/titanium carbide [Ti₃C₂]) can 99 promote electronic and/or compositional modifications of active catalytic sites and boost overall 100 activity, as demonstrated via the dehydrogenation reaction of light alkanes in an earlier study [16]. 101

We investigated the potential of Pt/Ti₃C₂ catalysts for RT oxidation of FA under dark conditions. 102 The effects of process variables, including the relative composition of Pt, catalyst mass (m_{cat}), flow 103 rate, FA concentration, relative humidity (RH), and time-on-stream (TOS), on FA oxidation were 104 evaluated. In situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) and density 105 functional theory (DFT) simulations were provided experimental and theoretical assessments of the FA 106 oxidation reaction pathway, RMSI, and the associated surface phenomena. This study aims to develop 107 a high-performance, non-oxide-supported Pt catalyst that does not require an alkali-metal promoter to 108 achieve high FA oxidation activity at RT. To the best of our knowledge, this study is the first attempt 109 to identify the potential utility of Pt/Ti₃C₂ as a RT thermal catalyst for VOC oxidation reactions under 110 dark conditions. 111

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113 2. Materials and methods

114 2.1. Chemical reagents

115 Quartz sand (SiO₂), paraformaldehyde (pFA; HO[CH₂O_nH]; 95%), and chloroplatinic acid 116 hexahydrate (H₂PtCl₆ · 6H₂O; \geq 37.5% Pt basis) were procured from Sigma-Aldrich (St. Louis, 117 Missouri, USA). Commercial Ti₃C₂ powder (> 98%) was purchased from Invisible Co., Ltd. (Suwon, 118 Republic of Korea). Two-dimensional Ti₃C₂ (MXene) was produced by traditional fluoride-based 119 etching of the aluminum layer in titanium carbo aluminide (Ti₃AlC₂) [20]. Air (99.999%), hydrogen 120 (H₂; 99.999%), and nitrogen (N₂; 99.999%) cylinders were procured from Union Gas Co., Ltd. (Yongin, 121 Republic of Korea).

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123 2.2. Catalyst synthesis

Synthesis of 0.1%, 1%, and 2% Pt/Ti₃C₂ catalysts employed a conventional incipient wetness 124 125 impregnation method [21]. Briefly, 76 mg of $H_2PtCl_6 \cdot 6H_2O$ was added to 20 mL of deionized (DI) H₂O (in a 100 mL glass beaker) and stirred at 500 rpm for 15 min at RT. Subsequently, 1 g of Ti₃C₂ 126 was added to the Pt solution and stirred at 500 rpm for 180 min at RT. The suspension was then placed 127 128 in an oven (ED-CO150, Han Yang Scientific Equipment Co., Ltd., Seoul, Republic of Korea), operating at 85°C for 15 h to evaporate the excess solvent and obtain the dry catalyst powder. The obtained 129 catalyst was labeled 2% Pt/Ti₃C₂. For synthesis of 0.1% and 1% Pt/Ti₃C₂, the amount of $H_2PtCl_6 \cdot 6H_2O$ 130 131 was adjusted to 3.8 mg and 38 mg, respectively, with the other procedures remaining the same.

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133 2.3. Temperature-programmed reduction experiments

The H₂ and carbon monoxide (CO) temperature-programmed reduction (TPR) experiments for the Ti₃C₂ and the Pt/Ti₃C₂ catalysts were performed using an AutoChem II instrument (Micromeritics Instrument Corp., Norcross, Georgia, USA). Loaded samples (80.4 ± 0.2 g) were treated by a flow of molecular oxygen (O₂; 5% in argon) with a total molar flow rate of 20 mL min⁻¹, while the temperature

was raised to 383.2 K at a rate of 10 K min⁻¹ to ensure full oxidation and removal of weakly adsorbed 138 species (e.g., CO₂ and H₂O) from the ambient air. The samples were then cooled to 303.2 K in a 50 mL 139 min⁻¹ argon flow to ensure all physically adsorbed oxygen was removed simultaneously. The heat was 140 then increased at 10 K min⁻¹ to 1,073 K under a flow of H_2 or CO in helium (0.10 mol⁻¹ and total flow 141 rate of 50 mL min⁻¹). A thermal conductivity detector (TCD) measured H₂ and CO consumption. The 142 total pressure during the reduction experiments was 107.1 ± 1.2 kPa. During H₂-TPR analysis, the 143 effluent was subcooled using isopropyl alcohol at -80°C to ensure the formed H₂O did not distort the 144 TCD signal while measuring H₂ consumption. During CO-TPR analysis, the TCD outlet signal was 145 146 corrected for the formation of CO₂ (see Supplementary Information [SI]).

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148 2.4. Formaldehyde catalytic oxidation experiments

All FA catalytic oxidation experiments were carried out using a tubular quartz fixed-bed reactor 149 (inner diameter and length of 0.4 and 11 cm, respectively) operating under atmospheric pressure [14]. 150 Catalyst powder (5 to 20 mg) mixed with SiO₂ (50 mg) was packed into the reactor using quartz wool 151 end plugs (Ohio Valley Specialty Company, Marietta, Ohio, USA). The fixed-bed temperature was 152 adjusted using an electric heater (TC200P [K], Misung Scientific Co., Ltd., Yangju, Republic of Korea). 153 Before the experiments, the fixed bed was conditioned at 300°C for 180 min under a flow (50 mL min⁻ 154 ¹) of either a mixture of H₂ (10%) + N₂ or N₂. In the case of the former, the suffix R was added to the 155 catalyst name (-R) to denote that it underwent thermal reduction pre-treatment. The gas was pulled 156 through the fixed bed using a vacuum pump (DOA-P704-AC, Gast Manufacturing Inc., Fair Plain, 157 Michigan, USA). The gas flow rate (50 to 250 mL min⁻¹) was adjusted using a control valve in 158 conjunction with a calibrator (FC-M1, Sibata Scientific Technology Ltd., Saitama, Japan). 159

A gaseous primary standard (G-PS) of FA was prepared through standard pFA thermal degradation 160 [22]. In brief, N₂ was pulled at 100 mL min⁻¹ through a quartz tube (maintained at 130°C) containing 161 pFA (100 mg) for 50 min. A 5 L polyester aluminum bag (Top Trading Co., Ltd., Seoul, Republic of 162 Korea) was utilized to collect the FA-rich effluent. The G-PS concentration was then determined using 163 standard 2,4-dinitrophenylhydrazine-based high-performance liquid chromatography [22]. An FA 164 gaseous working standard (G-WS) in a range of 100 to 735 ppm was then prepared by diluting the G-165 PS with air in a 100 L polyester aluminum bag. The RH in the as-prepared FA G-WS was expected to 166 be negligible. For catalysis in the presence of moisture, 680 to 2,000 μ L of DI H₂O was injected into 167 the 100 L G-WS bag using a 500 µL liquid-phase syringe (Trajan Scientific and Medical, Ringwood, 168 Australia) to produce an RH of 30%-90%. The FA G-WS was supplied to the fixed bed at 50-250 mL 169 \min^{-1} . 170

The fixed-bed temperature was ramped at 25°C intervals (starting from 30°C) until 100% FA 171 conversion (X_{FA}) was attained (Equation 1). [FA]_{in} and [FA]_{out} refer to concentrations measured at the 172 inlet and outlet of the fixed bed, respectively. The FA G-WS flow was maintained for at least 30 min 173 at each temperature point to ensure steady-state conditions. Both FA and CO₂ (produced via the deep 174 175 oxidation of FA) were quantified using a gas chromatograph (GC) equipped with a methanizer and flame ionization detector (FID) (iGC-7200, DS Science Inc., Gwangju, Republic of Korea). The FID, 176 methanizer, and GC oven temperatures were isothermally maintained at 280, 320, and 150°C, 177 respectively. The gas samples (500 µL) were injected into the GC using a gas-tight syringe (Trajan 178 Scientific and Medical, Ringwood, Australia). 179

The CO₂ yield (Y_{CO2}) was calculated using Equation 2 [23]. [CO₂]_{out} represents the CO₂ concentration at the fixed-bed outlet while $[CO_2]_t$ refers to the theoretical CO₂ concentration that should be produced through the deep oxidation of FA (based on the carbon balance). The steady-state reaction rate (r, in mol g⁻¹ h⁻¹) was calculated using Equation 3 [7]. F_{FA} represents the FA flow rate in mol s⁻¹. In the case of the FA (concentration = 100 ppm) adsorption experiment conducted at RT using the mixed $Ti_3C_2(120 \text{ mg})$ -SiO₂ (600 mg) bed, the breakthrough level (%) and adsorption capacity (q) (mg g⁻¹) were calculated using formulas reported in our previous work [24]. A Tensor II spectrometer (Bruker Corp., Billerica, Massachusetts, USA) equipped with an *in situ* diffuse-reflectance cell (Harrick Scientific Products, Inc., Pleasantville, New York, USA) was used for the *in situ* DRIFTS analysis [25]. The DRIFTS spectra were acquired at 30°C (in the dark) for two gaseous streams: FA + O₂ (1:1 mixture) and FA + He (1:1 mixture).

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$$X_{FA}(\%) = \left(\frac{[FA]_{in} - [FA]_{out}}{[FA]_{in}}\right) \times 100$$
 (1)

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$$Y_{CO_2}(\%) = \left(\frac{[CO_2]_{out}}{[CO_2]_t}\right) \times 100$$
 (2)

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$$r = \left(\frac{3,600 \times 10^3 \times X_{FA} \times F_{FA}}{m_{cat}}\right)$$
(3)

Internal mass and heat-transfer criteria were evaluated with respect to intrinsic kinetics (no significant influence of mass diffusion or temperature gradients in the catalytic material). As internal criteria are more stringent than external ones, only the former were evaluated effectively. Details of the implementation, calculation, and results of the internal mass and heat-transfer criteria are described in SI. We concluded that the required criteria were fulfilled, while no significant gradients occurred for the present catalytic experiments.

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201 *2.5. DFT method and model*

The Cambridge Serial Total Energy Package was used to conduct the DFT simulation [26, 27]. The exchange-correlation and interaction energy between electrons (e⁻) was processed using the Perdew– Burke–Ernzerhof (PBE) function under a generalized gradient approximation [28]. Interactions between the valence e⁻ and ionic nuclei was described in terms of ultra-soft pseudopotentials. The energy convergence criteria, maximum force, maximum displacement, plane wave cut-off energy, and

self-consistent field tolerance were set to 2×10^{-5} eV atom⁻¹, 0.05 eV Å⁻¹, 0.002 Å, 490 eV, and 2×10^{-5} eV atom⁻¹, 0.05 eV Å⁻¹, 0.002 Å, 490 eV, and 2×10^{-5} eV atom⁻¹, 0.05 eV Å⁻¹, 0.002 Å, 490 eV, and 2×10^{-5} eV atom⁻¹, 0.05 eV Å⁻¹, 0.002 Å, 490 eV, and 2×10^{-5} eV atom⁻¹, 0.05 eV Å⁻¹, 0.002 Å, 490 eV, and 2×10^{-5} eV atom⁻¹, 0.05 eV Å⁻¹, 0.002 Å, 490 eV, and 2×10^{-5} eV atom⁻¹, 0.05 eV Å⁻¹, 0.002 Å, 490 eV, and 2×10^{-5} eV atom⁻¹, 0.05 eV Å⁻¹, 0.002 Å, 490 eV, and 2×10^{-5} eV atom⁻¹, 0.05 eV Å⁻¹, 0.002 Å, 490 eV, and 2×10^{-5} eV atom⁻¹, 0.05 eV Å⁻¹, 0.002 Å, 490 eV, and 2×10^{-5} eV atom⁻¹, 0.05 eV Å⁻¹, 0.002 Å, 490 eV, and 2×10^{-5} eV atom⁻¹, 0.05 eV Å⁻¹, 0.002 Å, 490 eV, and 2×10^{-5} eV atom⁻¹, 0.05 eV Å⁻¹, 0.002 Å, 490 eV, atom⁻¹, 0.05 eV Å⁻¹, 0.002 Å, 0.000 eV 207 10⁻⁶ eV atom⁻¹, respectively, for the structural optimization of the model [29]. A 15 Å vacuum slab 208 separated the surface from its periodic image along the normal surface [30]. The bottom two layers 209 were constrained at the bulk position to mimic the larger number of layers in real metal particles, 210 whereas the upper two layers and the adsorbed species were allowed to relax. Brillouin zone-selected 211 k-point sampling of a Monkhorst-Pack scheme with a mesh size of $4 \times 4 \times 2$ was used to calculate the 212 density of states and e⁻ density [31]. The charge distribution was determined by Hirshfeld charge 213 analysis [32]. For a surface reaction such as $X + Y \rightarrow XY$, the reaction energy (ΔH) can be calculated 214 $(\Delta H = E_{XY} - E_X - E_Y)$ using the total energies (E) of the XY, X, and Y intermediates adsorbed on 215 Pt₃Ti [33]. Negative and positive ΔH values indicate exothermic and endothermic reactions, 216 respectively. The adsorption energy $(E_{ads} = E_A - E_B - E_C)$ describes the interactions between the 217 218 intermediates of the FA oxidation reaction and Pt₃Ti [34]. The terms E_A, E_B, and E_C represent the energy of the adsorbed intermediates, pristine Pt₃Ti, and the small molecules produced during the FA 219 oxidation reaction, respectively. 220

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222 **3. Results and discussion**

223 3.1. Physicochemical characterization

224 3.1.1. Physical characteristics

The physical properties of Ti₃C₂, Pt/Ti₃C₂, and 2% Pt/Ti₃C₂-R catalysts were analyzed using scanning electron microscopy (SEM), particle-size distribution analyses, transmission electron microscopy (TEM), selected area electron diffraction (SAED), powder X-ray diffraction (PXRD), thermogravimetric analyses (TGA), N₂ adsorption-desorption isotherms, pore-size distribution analyses, and inductively coupled plasma optical emission spectrometry (ICP-OES). The SEM image of Ti₃C₂ indicates that its distinctive accordion-like layered morphology closely matches those of earlier reports [16, 35] (Figure S1a). The Ti₃C₂ layers of the Pt/Ti₃C₂ catalysts were covered with irregular aggregates (e.g., the Pt oxide [PtO_x] species) (Figure S1b–d). The interlayer spacing of the MXene was also observed to decrease with an increase in Pt loading from 0.1% to 2% (Figure S1a– d). However, the average particle sizes of Ti₃C₂ and Pt/Ti₃C₂ catalysts ranged from 9 to 13 μ m (Figure S2a–d). The Pt loading therefore did not significantly alter Ti₃C₂ particle size (Figure S2a–d).

236 In the TEM image, the Ti_3C_2 layers are thin and transparent to e^- , with the appearance of multiple 237 stacked sheets (Figure S3a). The SAED pattern of Ti₃C₂ confirmed its single crystallinity and hexagonal symmetry [35] (inset of Figure S3a). The space parameter (d = 0.26 nm) evident in the 238 magnified TEM image of Ti₃C₂ corresponds to the (10-10) plane [36] (Figure S3b). The TEM image 239 of 2% Pt/Ti₃C₂ suggests tightly arranged Pt nanoparticles (NPs) aggregated in spherical clusters 240 (Figure S4a). The uniform arrangement of Pt NPs in 2% Pt/Ti₃C₂ reflects the prominent role of surface 241 functionalities and the RMSI in anchoring the noble-metal sites on the MXene surface (Section 3.1.2). 242 The similarity of the SAED patterns between 2% Pt/Ti₃C₂ and pristine Ti₃C₂ indicates that Pt loading 243 does not significantly alter the inherent MXene crystal structure (Figure S4a). The interplanar spacing 244 of 0.22 nm, which corresponds to the (111) facet of Pt, confirms the presence of crystalline Pt NPs 245 [37] (Figure S4b). The average Pt NP size for 2% Pt/Ti₃C₂ was 5.3 nm (Figure S5). 246

247 Reduction pre-treatment of 2% Pt/Ti₃C₂ resulted in the merging of individual Pt NPs to yield largely homogeneous particles approximately 50 nm in sized, which were identified as the Pt₃Ti IMC [15, 38, 248 39] (Figure S6a). High-temperature H₂-based reduction pre-treatment reportedly converts Pt/Ti₃C₂ 249 into Pt₃Ti IMC [15, 16]. The marked differences in the SAED pattern of 2% Pt/Ti₃C₂ before and after 250 the reduction indicate the formation of a Pt₃Ti IMC (polycrystalline due to the presence of both Pt₃Ti 251 and MXene) [38, 40] (Figure S6a). A magnified TEM image of 2% Pt/Ti₃C₂-R confirmed that the 252 Pt₃Ti particle should be bound to the surrounding material in a manner similar to that reported earlier 253 for such IMCs [38, 39] (Figure S6b). 254

The PXRD pattern for Ti₃C₂ displayed characteristic peaks at 20 values of 9°, 18.5°, 27.9°, and 255 60.7°, closely matching the (002), (006), (008), and (110) lattice planes of MXene, respectively [41] 256 (Figure 1a). No distinctive changes were evident in the PXRD patterns of 0.1%, 1%, and 2% Pt/Ti₃C₂ 257 258 when compared with pristine Ti₃C₂. As such, the Pt loading does not appear to alter the inherent crystal structure of MXene, which is consistent with the TEM results (Figure 1a). The characteristic Pt (111) 259 and (200) peaks (with corresponding 20 values of 39.2° and 45.7°, respectively) were not seen in the 260 PXRD patterns of the 0.1%, 1%, and 2% Pt/Ti₃C₂ catalysts, possibly due to low Pt loading [42] (Figure 261 1a). 262

The PXRD pattern of Pt₃Ti was reported to partially match that of auricupride (Cu₃Au) [15, 39] 263 (Figure S7). A polycrystalline structure of 2% Pt/Ti₃C₂-R is evident with the presence of characteristic 264 peaks for both MXene and Pt₃Ti in its PXRD analysis (Figure 1b). Its polycrystalline structure is 265 supported further by the mismatch in Pt₃Ti peak intensities between 2% Pt/Ti₃C₂-R and the simulated 266 Cu₃Au (Figure 1b). A higher reduction temperature (e.g., up to 550°C) is often required to fully convert 267 Pt/Ti₃C₂ to Pt₃Ti, as demonstrated in earlier works [15, 16]. One of the objectives of the present work 268 269 was to avoid excess heat requirements for pre-treatment to lower the preparation cost of catalyst and 270 to demonstrate the suitability of the lowered reduction temperature (for substantially high FA oxidation performance). Hence, the use of lower reduction temperature (e.g., 300°C) in the present work was 271 validated for the production of a polycrystalline catalyst with Pt₃Ti sites supported by the MXene in 272 line with the above discussions. 273

In TGA profiles, Ti_3C_2 displayed three distinct regions of mass loss removal of physisorbed moisture and fluorine from the MXene surface (RT–210°C), removal of chemisorbed H₂O from the MXene structure (210°C–620°C), and oxygen and fluorine removal from the MXene structure (> 620°C) [43] (Figure 1c). Overall, Ti_3C_2 exhibited relatively high thermal stability as it lost only approximately 25% of its mass at temperatures between RT and 800°C (Figure 1c). The Pt/Ti₃C₂ catalysts displayed improved thermal stabilities compared to pristine Ti₃C₂, losing only approximately

10% of their mass in the RT-800°C range (Figure 1c). The enhanced thermal stability of Pt/Ti₃C₂ over 280 pristine Ti₃C₂ reflects strong Pt-MXene interactions, which make the liberation of oxygen, H₂O, and 281 fluorine-containing groups from the MXene structure energetically taxing [43]. Also, the Pt/Ti₃C₂ 282 catalysts underwent a heat treatment during the drying process (see Section 2.2) that might have led 283 to weight loss in the TGA profile (e.g., relative to Ti_3C_2) by removing some of the H₂O from the 284 MXene structure. Furthermore, as the samples were not subjected to any pre-treatments before the 285 TGA, it might have influenced the amount of moisture and other impurities retained on the surfaces 286 of the samples to cause biases in the TGA result. Notably, the thermal stability of 2% Pt/Ti₃C₂-R was 287 enhanced compared with its non-reduced counterpart, possibly because a large amount of chemisorbed 288 H₂O was already removed from the MXene structure during reduction pre-treatment (Figure S8). 289

The occurrences of a type-IV-like pattern, observed from N2 adsorption-desorption isotherms of 290 Ti₃C₂, Pt/Ti₃C₂ catalysts, and 2% Pt/Ti₃C₂-R, indicate their primarily mesoporous nature [44] (Figure 291 1d). The low P/P_0 region of the N₂ adsorption-desorption isotherm suggests complete filling of the 292 micropores. The moderate P/P₀ region of the N₂ adsorption-desorption isotherm denotes the mono-293 294 and multilayered adsorption of N₂ molecules. The existence of a hysteresis loop at the high P/P₀ region 295 may reflect the capillary condensation of N₂ molecules into the mesopores [44]. The H3-type hysteresis loop in the N₂ adsorption-desorption isotherm of all the tested materials (Figure 1d) 296 indicates the presence of slit-like pores originating from the loose assemblages (aggregates) of plate-297 like particles [45]. 298

The prominence of the hysteresis loop in Ti_3C_2 and 2% Pt/ Ti_3C_2 -R relative to the Pt/ Ti_3C_2 catalysts suggests a larger volume of mesopores in the former structures (Figure 1d). This was confirmed when plotting the pore-size distribution of the analyzed materials (Figure S9). As shown in Figure S9, Ti_3C_2 has a much larger volume of mesopores in the 2–4 nm range compared with Pt/ Ti_3C_2 catalysts. Also, a relatively large number of pores in the 1–4 nm range can be found in 2% Pt/ Ti_3C_2 (Figure S9). All the analyzed materials contained some micropores between 0.9 and 2 nm in size, which is consistent

with the patterns of N₂ adsorption-desorption isotherms as described above (Figure S9). Brunauer-305 Emmett-Teller (BET) surface area/pore-volume and Barrett-Joyner-Halenda average pore-diameter 306 values for Ti₃C₂ and Pt/Ti₃C₂ catalysts are summarized in Table 1. The BET surface area and pore 307 volume of 2% Pt/Ti₃C₂-R were 6.1 and 5.4 times higher, respectively, compared with 2% Pt/Ti₃C₂, 308 due to defects in the MXene structure or conversion of Pt species to Pt₃Ti brought about by reduction 309 pre-treatment (Table 1). Nevertheless, the average pore diameter did not change substantially after 310 reduction pre-treatment (Table 1). The actual Pt content in the catalyst samples, as quantified using 311 ICP-OES, is listed in Table 1. Good compatibility between the theoretically predicted and 312 experimentally determined Pt amounts was observed for all the Pt/Ti₃C₂ catalysts (Table 1). 313

Results of the TPR experiments are provided in Table 2 and Figure 2. For the MXene, comparable 314 quantities of oxygen were used in the reduction during CO-TPR and H₂-TPR experiments, namely 315 $7.60 \pm 0.40 \ \mu mol_{O}$ and $8.31 \pm 1.71 \ \mu mol_{O}$, respectively. For a catalyst load of 80 mg, both the above 316 values correspond to approximately 10^{-1} mol_O kg_{cat}⁻¹. Comparable oxygen concentrations (C_O) have 317 been reported in the literature [46]. Particularly noteworthy is the observation that the Pt-containing 318 catalysts displayed much higher C₀. For CO-TPR, both 2% Pt/Ti_3C_2 and 2% Pt/Ti_3C_2 -R have values 319 of $2.48 \pm 0.09 \times 10^{-1} \text{ mol}_{O} \text{ kg}_{\text{cat}}^{-1}$ and $4.49 \pm 0.70 \times 10^{-1} \text{ mol}_{O} \text{ kg}_{\text{cat}}^{-1}$, respectively, whereas the H₂-TPR 320 consumed $4.05 \pm 0.11 \times 10^{-1} \text{ mol}_{O} \text{ kg}_{cat}^{-1}$ for 2% Pt/Ti₃C₂ and $3.35 \pm 0.27 \times 10^{-1} \text{ mol}_{O} \text{ kg}_{cat}^{-1}$ for 2% 321 Pt/Ti_3C_2 -R. 322

For the CO-TPR data, the reduction peaks for the carrier material were observed in the $150-350^{\circ}C$ range, whereas for the Pt-containing catalysts, the peaks were visible between $150-550^{\circ}C$. The above observations indicate the possible formation of reducible O_{ads} species due to the presence of the Pt on the MXene surface. Comparing the 2% Pt/Ti₃C₂ and 2% Pt/Ti₃C₂-R catalysts, the low-temperature peaks (below $350^{\circ}C$) contributed 27% and 92% to the total signal, respectively. The higher concentration of oxygen available for reduction may explain the superior performance of the reduced catalyst (Section 3.2). The first peak-reduction temperature for 2% Pt/Ti₃C₂ (187.4°C) was lower than that of the carrier material (191.6°C), explaining the catalytic activity at low temperatures (Section 3.2). However, the 2% Pt/Ti₃C₂-R (217.6°C) peak-reduction temperature was significantly higher. On the other hand, the contribution to the total signal of reducible oxygen atoms was higher on the latter sample (21%) than the former (8%) to explain the superior activity of the latter (Section 3.2).

For the H₂-TPR data, reduction peaks for the carrier material were observed in the 170–600°C 334 range, whereas for the Pt-containing catalysts, peaks were visible between 35°C and 600°C. This 335 suggests the formation of active oxygen (O*) due to the presence of Pt on the surface, as was the case 336 for CO-TPR. In addition, there was a shift in reduction temperature, i.e., H₂ required higher reduction 337 temperatures for the carrier material. However, lower reduction temperatures were observed when Pt 338 was present on the surface. The high-temperature peaks (> 350°C) represented approximately 17% of 339 the total signal for the Pt catalysts, whereas, for the carrier material, this value was approximately 70%. 340 The first peak-reduction temperature for 2% Pt/Ti₃C₂ (85.8°C) was significantly lower than for the 341 carrier material (269.5°C), explaining the excellent catalytic activity at low temperatures (see Section 342 3.2). The first peak-reduction temperature for 2% Pt/Ti₃C₂-R (67.6°C) was even lower than for the 343 non-reduced sample. Given the fact that the contribution to the total signal of reducible oxygen atoms 344 was lower in the latter sample (2%) than in the former (6%), the presence of easily replaceable oxygen 345 species explains the superior catalytic activity of the 2% Pt/Ti₃C₂-R catalyst (see Section 3.2). 346

For the CO-TPR results (Figure 2), additional peaks at high temperatures (> 350° C) were observed, compared with the carrier material, accounting for 73% and 9% of the total signal for 2% Pt/Ti₃C₂ and 2% Pt/Ti₃C₂-R, respectively. The amounts of oxygen used for the reduction were 19.9 ± 0.7 and $36.5 \pm 5.6 \mu$ mol₀, respectively. The reduction pre-treatment in catalyst preparation significantly shifted O* surface species toward lower reduction temperatures. For the H₂-TPR results, the high-temperature peaks decreased after Pt deposition with three peaks in the high-reduction-temperature region. In 353 contrast, one of these peaks appears to have completely shifted toward the low-temperature range for354 the Pt-containing catalysts.

As seen in the H₂-TPR data, no significant distinction in the total amount of reducible oxygen on 355 both the catalysts (~ 0.40 molo kg_{cat}⁻¹ for 2% Pt/Ti₃C₂ and 2% Pt/Ti₃C₂-R (Table 2)) may be indicative 356 357 of the (strong) reducing power of H₂. For the CO-TPR data, the amount of reducible oxygen on 2% Pt/Ti₃C₂ catalyst (~ 0.25 molo kg_{cat}⁻¹) is approximately half of that on the 2% Pt/Ti₃C₂-R catalyst, 358 while the peaks of the former occur at higher reduction temperatures (72% of the signal is situated 359 after 350°C). For the 2% Pt/Ti₃C₂-R catalyst, a comparable amount of reducible oxygen is titrated (~ 360 0.40 mol_o kg_{cat}⁻¹), although it also occurs at a higher temperature than those of H₂-TPR on 2% 361 Pt/Ti₃C₂-R. Likewise, if the poorer reduction power of CO is granted, the same reducible oxygen is 362 suspected to be reduced at higher temperatures. Hence, the strength of the reducing gas explains the 363 shift towards higher reduction peak temperatures in the CO-TPR on 2% Pt/Ti $_3C_2$. For the 2% Pt/Ti $_3C_2$ -364 R catalyst, 91% of the signal present in the low-temperature range indicate the beneficial effect of 365 reduction pre-treatment in catalyst synthesis. However, the corresponding peak temperatures are still 366 lower for H₂-TPR. 367

Lastly, a remarkable linear relation (a slope of close to 1) was found between the peak-reduction temperatures for the 2% Pt/Ti₃C₂-R and 2% Pt/Ti₃C₂ for both CO-TPR and H₂-TPR (Figure 3a). Comparing the reduction temperatures for both catalysts to the values for the carrier material (by ranking the peak temperatures in increasing order), CO-TPR required equal or higher temperatures. In contrast, for H₂-TPR, the opposite result was obtained, i.e., Pt-containing catalysts required lower reduction temperatures (Figures 3b and c).

374

375 *3.1.2. Surface chemistry*

376 Energy-dispersive X-ray spectroscopy (EDX) mapping was used to assess the distribution of elements on the surfaces of Ti₃C₂ and Pt/Ti₃C₂ catalysts (Figure S10). As expected, the Ti₃C₂ surface 377 was primarily comprised of titanium (Ti) and oxygen species (Figure S10a). In the EDX mapping, 378 379 carbon was not considered to avoid confusion because of a conductive carbon adhesive tape used for the EDX measurements. In the case of Pt/Ti₃C₂ catalysts, chlorine (Cl) was present alongside the Ti 380 and oxygen species (Figure S10b-d). The presence of Cl on the Pt/Ti₃C₂ surface should reflect the use 381 382 of $H_2PtCl_6 \cdot 6H_2O$ for the impregnation of Pt on the catalyst surfaces. In line with the Pt content of the catalysts, the Cl amounts on the 1% and 2% Pt/Ti₃C₂ surfaces were higher than that on 0.1% Pt/Ti₃C₂ 383 (Figures S10b-d). As the test samples were coated with Pt for the EDX analysis, Pt was not considered 384 in the EDX mapping to avoid confusion. 385

X-ray photoelectron spectroscopy was utilized to assess the electronic states of the elements present 386 on the Ti₃C₂ and Pt/Ti₃C₂ catalyst surfaces and to confirm the presence of RMSI. The deconvoluted 387 core-level Ti 2p spectrum of Ti₃C₂ confirmed the presence of Ti-C, Ti²⁺, and Ti³⁺ doublet peaks [15] 388 (Figure 4a). The surface ratios of Ti-C/Ti, Ti^{2+}/Ti , and Ti^{3+}/Ti for $Ti_{3}C_{2}$ were 37.1%, 21.5%, and 41.4%, 389 respectively (Figure 4a). For 0.1% Pt/Ti₃C₂, a characteristic signal for Ti⁴⁺ species was detected 390 alongside Ti-C, Ti²⁺, and Ti³⁺ in the core-level Ti 2p spectrum. The presence of such signals indicate 391 possible alterations in the Ti electronic environment due to the presence of Pt [15] (Figure 4b). The 392 surface ratios of Ti-C/Ti, Ti²⁺/Ti, Ti³⁺/Ti, and Ti⁴⁺/Ti for 0.1% Pt/Ti₃C₂ were 11.6%, 27.5%, 22.6%, 393 and 38.4%, respectively (Figure 4b). All the Ti-C, Ti²⁺, and Ti³⁺ peaks displayed blue shifts (increased 394 binding energy) between +0.1 and +1.1 eV range compared with pristine Ti₃C₂. These blue shifts 395 should reflect the oxidation of the MXene support due to the RMSI [16, 47] (Figure 4b). The surface 396 ratios of Ti-C/Ti, Ti²⁺/Ti, Ti³⁺/Ti, and Ti⁴⁺/Ti for 1%-Pt/Ti₃C₂ were determined to be 9.7%, 18.9%, 397 24.5%, and 46.9%, respectively (Figure 4c). Their counterparts for 2% Pt/Ti₃C₂ were 15.1%, 21.3%, 398 13%, and 50.6%, respectively (Figure 4d), indicating that Ti^{4+} species in the Pt/Ti₃C₂ catalyst tend to 399 rise with increased Pt loading due to enhanced RMSI and oxidation of the MXene support [47, 48]. 400

401 The deconvoluted core-level C 1s spectrum of Ti₃C₂ revealed the presence of C-Ti (282.1 eV), C-C (285.1 eV), C-O (287.2 eV), and O-C=O (289.1 eV) species [48] (Figure S11a). The surface ratios 402 of C-Ti/C, C-C/C, C-O/C, and O-C=O/C for Ti₃C₂ were estimated to be 22.1%, 67.8%, 3.7%, and 403 404 6.4%, respectively (Figure S11a). Although the C-Ti peak position did not shift for the Pt/Ti₃C₂ catalysts, an O-C=O peak was observed at 289.2 eV (a blue shift of +0.1 eV) for the 0.1%, 1%, and 405 2% Pt/Ti₃C₂ catalysts. Such an observation indicates alterations in the local electronic environment 406 (Figure S11b-d). Decreases in C-Ti/C surface ratio for the 0.1%, 1%, and 2% Pt/Ti₃C₂ catalysts (such 407 as 12.8%, 11.3%, and 7.7%, respectively) further indicate increased oxidation of MXene support and 408 increased Pt loading due to the RMSI [47, 48] (Figure S11b-d). 409

The deconvoluted core-level O 1s spectrum of Ti₃C₂ revealed the presence of Ti-O (530 eV), C-Ti-410 (OH)_x (531.9 eV), and adsorbed H₂O (H₂O_{ads} at 534 eV) species [49, 50] (Figure S12a). The shifts in 411 Ti-O peaks to a higher binding energy (a blue shift of +0.7 to +0.8 eV) in the Pt/Ti₃C₂ catalysts further 412 indicate the oxidation of MXene support due to Pt impregnation (RMSI) (Figures S12b-d). Unlike 413 Ti₃C₂, Pt/Ti₃C₂ catalysts displayed only two peaks in the core-level O 1s spectrum (Figures S12b-d). 414 The higher binding energy peaks at 532.5, 532.4, and 532.3 eV in the deconvoluted core-level O 1s 415 spectra of the 0.1%, 1%, and 2% Pt/Ti₃C₂ catalysts can be attributed to the lumped C-Ti-(OH)_x, H₂O_{ads}, 416 and adsorbed oxygen species (O_{ads} [O⁻, O₂⁻, and O₂²⁻]), respectively (Figures S12b–d). While the 417 proximity of individual O 1s peaks make it difficult to distinguish clear signals for each component in 418 the core-level O 1s XPS spectrum [51], it is likely that the Pt catalysts possess O_{ads} on their surfaces, 419 as the noble-metal sites generate O^- , O_2^- , and O_2^{2-} species, leading to dissociative adsorption of O_2 420 molecules [42]. 421

The deconvoluted core-level Pt 4f spectrum of 0.1% Pt/Ti₃C₂ indicates the presence of characteristic 4f_{5/2} (75.7 eV) and 4f_{7/2} (71.7 eV) doublet peaks, with the Pt species existing only in metallic form (Pt⁰) [52] (Figure 5a). In addition to the Pt⁰ species, Pt²⁺ species were observed in both 1% and 2% Pt/Ti₃C₂ [53] (Figure 5b and c). The Pt⁰/Pt surface ratio for the 0.1%, 1%, and 2% Pt/Ti₃C₂

catalysts were 100%, 78.4%, and 28.9%, respectively (Figure 5a-c). An increase in Pt loading resulted 426 in a simultaneous increase in the amount of Pt^{2+} species (Figure 5a–c). Note that the $4f_{7/2}Pt^{2+}$ peak for 427 the 1% Pt catalyst could not be explicitly marked on the deconvoluted graph due to its relatively small 428 size. However, it is expected to be present since the Pt^{2+} peaks usually occur as doublets (Figure 5b). 429 The $4f_{7/2}$ Pt⁰ peak displayed a redshift (lowering of binding energy of -0.2 and -0.5 eV for 1%, and 430 2% Pt/Ti₃C₂ catalysts, respectively, compared to 0.1% Pt/Ti₃C₂ (Figure 5a-c). The 4f_{5/2} Pt⁰ peak also 431 displayed a redshift of -0.9 and -1 eV for 1%, and 2% Pt/Ti₃C₂ catalysts, respectively, compared to 432 0.1% Pt/Ti₃C₂ (Figure 5a-c). Also, the $4f_{5/2}$ Pt²⁺ peak of 1%-Pt/Ti₃C₂ exhibited a redshift of -1.1 eV 433 when the Pt content increased to 2% (Figure 5b and c). The occurrences of red-shifting phenomena in 434 the Pt peak position imply reduction of noble-metal sites (simultaneous oxidation of the MXene 435 support, as described above) due to the RMSI [47]. 436

The deconvoluted core-level Ti 2p spectrum of 2% Pt/Ti₃C₂-R indicates the presence of Ti²⁺ (459.6 437 eV), Ti^{3+} (460.3 eV), and Ti^{4+} (465.3 and 472.8 eV) species (Figure 6a). The surface ratios of Ti^{2+}/Ti , 438 Ti^{3+}/Ti , and Ti^{4+}/Ti for 2% Pt/Ti₃C₂-R were 41.5%, 22.9%, and 35.7%, respectively (Figure 6a). The 439 disappearance of the Ti-C peak in the core-level Ti 2p spectrum of 2% Pt/Ti₃C₂-R indicates the 440 formation of a Pt₃Ti IMC through reduction pre-treatment (transformation of the MXene structure, as 441 described in Section 3.1.1) [15, 16] (Figure 6a). The Ti²⁺, Ti³⁺, and Ti⁴⁺ peaks in the core-level Ti 2p 442 spectrum of 2% Pt/Ti₃C₂-R displayed blue shifts between +2.5 and +7.4 eV (compared to 2% Pt/Ti₃C₂) 443 (Figure 6a). The blue shifts in the Ti peak positions indicate the lowering of e⁻ density in the local 444 electronic environment of the Ti species after reduction pre-treatment (e.g., oxidation and 445 transformation of the MXene support) [15, 54]. 446

447 The deconvoluted core-level C 1s spectrum of 2% Pt/Ti₃C₂-R revealed the presence of C-C (285.5

448 eV), C-O (287.3 eV), and O-C=O (289.2 eV) species (Figure 6b). The surface ratios of C-C/C, C-O/C,

- 449 and O-C=O/C for 2% Pt/Ti₃C₂-R were 78.8%, 9.5%, and 11.7%, respectively (Figure 6b). A
- 450 deconvoluted core-level O 1s spectrum of 2% Pt/Ti₃C₂-R revealed the presence of Ti-O (530.8 eV),

451 O_{ads}/C -Ti-(OH)_x (531.2 eV), and H₂O_{ads} (533.2 eV) (Figure 6c). The surface ratios of Ti-O/O, O_{ads}/C -452 Ti-(OH)_x/O, and H₂O_{ads}/O for 2% Pt/Ti₃C₂-R were 49.9%, 30.3%, and 19.8%, respectively (Figure 453 6c). The deconvoluted core-level Pt 4f spectrum of 2% Pt/Ti₃C₂-R included peaks for 4f_{7/2} (71.3 eV) 454 and 4f_{5/2} (74.7 and 76.6 eV) (Figure 6d). The 4f_{7/2} and 4f_{5/2} peaks in the core-level Pt 4f spectrum of 455 2% Pt/Ti₃C₂-R displayed blue shifts between +0.1 and +1.2 eV (compared to 2% Pt/Ti₃C₂) (Figure 456 6d). The blue shifts in the Pt peak positions indicate formation of Pt₃Ti IMC [55].

457

458 *3.2. FA removal performance evaluation*

The light-off curves of the analyzed catalysts illustrate the relative performance of FA oxidation in 459 the following order: $2\% \text{ Pt/Ti}_3\text{C}_2\text{-R} > 1\% \text{-Pt/Ti}_3\text{C}_2\text{-R} > 0.1\% \text{ Pt/Ti}_3\text{C}_2\text{-R} > 2\% \text{ Pt/Ti}_3\text{C}_2$ (Figure 7a). 460 461 The close tracking of Y_{CO2} with X_{FA} observed from all the tested catalysts suggests the complete mineralization of FA in accord with the carbon balance (Figure 7a). The r values (at RT) for 2% 462 Pt/Ti₃C₂-R, 1%-Pt/Ti₃C₂-R, 0.1% Pt/Ti₃C₂-R, and 2% Pt/Ti₃C₂ were 0.061, 0.058, 0.054, and 0.02 mol 463 g⁻¹ h⁻¹, respectively (Table 3). The performance (r value at RT) of 2% Pt/Ti₃C₂-R was 3.1 times greater 464 than its non-reduced counterpart, i.e., 2% Pt/Ti₃C₂ (Table 3). The T₅₀ and T₉₀ values (reaction 465 temperatures corresponding to 50% and 90% X_{FA}, respectively) for the Pt/Ti₃C₂ catalysts are also 466 467 provided in Table 3.

These results indicate that pre-treatment reduction dramatically enhances catalytic activity, possibly through the formation of Pt₃Ti IMC (see Sections 3.1 and 3.3.2). In addition, an increase in Pt loading should enhance catalytic activity, possibly due to increases in the active site-to-pollutant ratio. Consistent with general expectations, Ti₃C₂ did not exhibit catalytic behavior on its own at RT, as the breakthrough level of 100 ppm FA rose steadily to reach 100% within the first 25 min under operating conditions of a flow rate of 50 mL min⁻¹, total bed mass of 720 mg (120 mg of Ti₃C₂ + 600 mg of SiO₂), and 0% RH (Figure S13). A maximum q value for FA (0.07 mg g⁻¹) was obtained for the physically mixed Ti₃C₂-SiO₂ fixed bed (Figure S13). The highest-performing catalyst, as measured by
the effect of process variables on the FA removal performance in terms of the r value at RT, was 2%
Pt/Ti₃C₂-R, which was used for the leveled-up stages of experiments.

A decrease in the RT X_{FA} value was apparent for 2% Pt/Ti₃C₂-R in the form of lower m_{cat} values 478 (X_{FA} of 100%, 75%, and 65% for 20, 10, and 5 mg m_{cat}, respectively) (Figure 7b). This may reflect a 479 480 decline in the number of active surface sites for FA oxidation. The inverse relationship between the 481 gas hourly space velocity (GHSV) and m_{cat} may also reflect the effect of shortened contact time between FA molecules and active catalytic sites. Likewise, the lowering of the RT X_{FA} value with an 482 increased flow rate (e.g., X_{FA} of 100%, 85%, and 57% for the flow rate of 50, 100, and 250 mL min⁻¹, 483 respectively) should reflect a decline in the FA residence time of 2% Pt/Ti₃C₂-R (increases in GHSV) 484 within the fixed-bed reactor (Figure 7c). The 2% Pt/Ti₃C₂-R maintained 100% X_{FA} (at RT) up to 250 485 ppm FA (Figure 7d). The X_{FA} (at RT) then declined with a further increase in FA concentration (X_{FA} 486 of 78 and 61% for 610 and 735 ppm FA, respectively) (Figure 7d). The lowering of X_{FA} at elevated 487 FA concentrations should be induced by the saturation of the active surface sites due to a reduced 488 active site-to-FA ratio [56]. 489

The presence of atmospheric water molecules can impede catalytic reactions as they compete with 490 491 the target pollutants for active surface sites. It is therefore surprising to find that 2% Pt/Ti₃C₂-R retained 100% X_{FA} over the entire tested range of RH (0%–90%) (Figure 7e). This suggests that 492 moisture does not interfere with catalytic FA oxidation on a 2% Pt/Ti₃C₂-R surface. The maintenance 493 494 of 100% X_{FA} over such a wide RH range indicates that 2% Pt/Ti₃C₂-R can operate effectively under even harsh real-world conditions (Figure 7e). The mixed Ti and Pt structures of Pt₃Ti IMC selectively 495 adsorbed the carbonyl (C=O) group of FA, achieving complete degradation under humid conditions. 496 The catalytic durability and stability of 2% Pt/Ti₃C₂-R were also determined for the RT oxidative 497 removal of FA in the air (Figure 7f). A conversion rate of 100% X_{FA} to CO₂ was stably maintained for 498

the maximum tested duration of 50 h TOS without any deactivation under optimized processconditions.

501

502 *3.3. FA oxidation pathway and mechanism*

503 3.3.1. In situ DRIFTS and physicochemical characterization

In situ DRIFTS spectra were acquired both in the presence and absence of O₂ to estimate the 504 possible pathways of FA oxidation on 2% Pt/Ti₃C₂-R (Figures 8 and S14). The following species were 505 506 observed in the *in situ* DRIFTS spectrum during the oxidation of FA in the presence of O₂: (i) molecularly adsorbed FA (FA_{ads} [1632–1888 cm⁻¹]), (ii) dioxymethylene (H₂CO₂ [DOM; 1125 vCO 507 and 1358–1585 cm⁻¹ δ CH₂, ω CH₂, and ν OCO]), (iii) formate (HCOO⁻ [1358–1585 δ CH, 508 509 symmetric/asymmetric OCO vibrational modes [$v_sOCO/v_{as}OCO$] of bidentate HCOO⁻, and v_sOCO of monodentate HCOO⁻, 1632–1888 [v_{as}OCO of monodentate HCOO⁻], and 3089–3225 cm⁻¹ vCH), (iv) 510 linearly adsorbed CO (2170 cm⁻¹), (v) molecularly adsorbed H₂O (H₂O_{ads} [3089–3225 cm⁻¹]), (vi) 511 surface OH (3089–3225 cm⁻¹), and (vii) CO_2 (2343 and 2368 cm⁻¹) [10] (Figure 8). These observations 512 indicate that FA molecules are first adsorbed on the catalyst surface (Section 3.3.2) and subsequently 513 oxidized to CO_2 and H_2O via DOM, $HCOO^-$, and CO intermediates (Equation 4). 514

515 $FA \rightarrow FA_{ads} \rightarrow DOM \rightarrow HCOO^{-} \rightarrow CO \rightarrow CO_2 + H_2O_{ads}$ (4)

The formation of DOM, HCOO⁻, and CO intermediates in a He environment suggests a potent role for O^{*} on the 2% Pt/Ti₃C₂-R surface in oxidation of FA_{ads} species [57, 58] (Figure S14). FA_{ads} may interact with O^{*} to form DOM, which then dissociates or combines with O^{*} to yield HCOO⁻ [59]. As the HCOO⁻ decomposes into CO, it combines with O^{*} to form a CO₂ end product. The decomposition of HCOO⁻ can also produce H₂O_{ads} alongside CO₂. The consumed O^{*} will then be replenished through dissociative adsorption of O₂ to sustain the net catalytic reaction. An FA oxidation reaction in the absence of O₂ is unlikely to be sustained over prolonged periods [58].

After 50 h of TOS FA oxidation, physicochemical analyses of the 2% Pt/Ti₃C₂-R samples was 523 conducted to examine the stability of the Pt₃Ti IMC. Dramatic changes in the PXRD pattern of 2% 524 Pt/Ti₃C₂-R observed after FA oxidation may indicate alterations in its crystal structure (Figure S15). 525 The intensity of the prominent Pt₃Ti peak at 25.2° was reduced significantly after such reactions 526 (Figure S15). Similarly, the intensities of the Pt₃Ti peaks at 48.1°, 55.1°, 62.8°, 70.5°, and 75.1° 527 decreased after FA oxidation (Figure S15). In contrast, the intensities of the characteristic MXene 528 peaks at 9°, 18.5°, and 60.7° increased after FA oxidation (Figure S15). Oxidation of FA may have 529 led to the conversion of the 2% Pt/Ti₃C₂-R structure back to its non-reduced form (Section 3.3.2). It is 530 therefore possible that pre-treatment reduction could be used to recover Pt₃Ti IMC once the catalyst 531 deactivates completely. 532

The deconvoluted Ti 2p core-level XPS spectrum of 2% Pt/Ti₃C₂-R obtained after the FA oxidation 533 indicates the existence of four types of Ti species (Ti-C, Ti²⁺, Ti³⁺, and Ti⁴⁺) similar to 2% Pt/Ti₃C₂ 534 (Figure S16a). The surface ratios of Ti-C/Ti, Ti²⁺/Ti, Ti³⁺/Ti, and Ti⁴⁺/Ti for 2% Pt/Ti₃C₂-R after FA 535 oxidation were 10.2%, 32.7%, 30%, and 27.1%, respectively (Figure S16a). The peaks in the Ti 2p 536 core-level XPS spectrum of 2% Pt/Ti₃C₂-R displayed blue shifts between +0.1 and +7 eV after FA 537 oxidation when compared to the 2% Pt/Ti₃C₂ XPS spectrum. The XPS data also indicate that the Pt₃Ti 538 structure reverted to a non-reduced state (2% Pt/Ti₃C₂) after FA oxidation, consistent with the PXRD 539 results. 540

The deconvoluted C 1s core-level XPS of 2% Pt/Ti₃C₂-R after FA oxidation indicates the presence of four types of carbon species (C-Ti, C-C, C-O, and O-C=O), similar to 2% Pt/Ti₃C₂ (Figure S16b). The surface ratios of C-Ti/C, C-C/C, C-O/C, and O-C=O/C for 2% Pt/Ti₃C₂-R after FA oxidation were 9%, 73.3%, 6.9%, and 10.7%, respectively (Figure S16b). The deconvoluted core-level 2% Pt/Ti₃C₂-R O 1s spectrum after FA oxidation indicate the presence of two types of oxygen species (Ti-O and O_{ads}/H₂O_{ads}/C-Ti-(OH)_x), similar to 2% Pt/Ti₃C₂ (Figure S16c). The surface ratios of Ti-O/O and 547 O_{ads}/H₂O_{ads}/C-Ti-(OH)_x/O for 2% Pt/Ti₃C₂-R after FA oxidation were 39.7% and 60.3%, respectively
548 (Figure S16c).

On similar lines, the deconvoluted core-level 2% Pt/Ti₃C₂-R Pt 4f spectrum after FA oxidation 549 indicates the presence of two Pt species (Pt⁰ and Pt²⁺), similar to 2% Pt/Ti₃C₂ (Figure S16d). This 550 further indicates that the Pt₃Ti IMC structure should be dismantled to revert to the Pt NP form through 551 oxidation FA, after which the Pt⁰/Pt and Pt²⁺/Pt surface ratios for 2% Pt/Ti₃C₂-R were 43.6 and 56.3%, 552 respectively (Figure S16d). The amount of Pt⁰ species in 2% Pt/Ti₃C₂-R after FA oxidation was 1.5 553 times greater than in 2% Pt/Ti₃C₂ (Figure S16d). The Pt⁰ and Pt²⁺ peaks for 2% Pt/Ti₃C₂-R also 554 displayed blue shifts between +0.1 and +0.5 eV after FA oxidation when compared to the peaks in the 555 2% Pt/Ti₃C₂ XPS spectrum (Figure S16d). 556

To further observe the variations in the morphology of 2% Pt/Ti₃C₂-R after FA oxidation, the TEM images were analyzed (Figure S17a and b). The Pt₃Ti IMC structure appeared to be gradually dismantling and reverting to its non-reduced form, i.e., similar to the Pt NPs in 2% Pt/Ti₃C₂ (Figure S17a and b). The SAED pattern further indicated that reversion of 2% Pt/Ti₃C₂-R to a pre-reduction state was incomplete after 50 h of TOS FA oxidation, which is consistent with the above observations (Figure S17a). It is therefore likely that the durability and practicality of Pt₃Ti IMC are sufficient realworld applications.

564

565 *3.3.2. DFT simulation*

A theoretical model was established for FA oxidation based on previous studies of Pt_3Ti and other supported NPs on 2D transition-metal carbides involving metal-support interactions (MSIs) [15, 29, 38, 60-66] (Figure 9a–c). Figure 9a shows the atomic structure of Pt_3Ti , in which the Ti-Pt and Pt-Pt bond lengths are 2.785 and 2.723 Å, respectively. The green hexagonal dotted-line box reflects the unique six-coordination structure of Pt_3Ti . The closely packed model in Figure 9d–e more intuitively shows the morphology of metal Pt_3Ti clusters. Based on the structure of the catalyst active material obtained in the experiment, we selected three adsorption sites according to the characteristics of the atomic chemical position on the Pt_3Ti surface.

Detailed adsorption data for the small intermediate molecules in the process of FA catalytic 574 oxidation to CO₂ and H₂O are shown in Table 4. The adsorption energy of FA on the Pt₃Ti surface 575 was -1.72 eV, which corresponds to an adsorption distance of 2.04 Å. During the activation process, 576 577 FA receives 0.25 e⁻ from Ti and Pt atoms. These results show that FA can be stably chemisorbed on the Pt₃Ti surface. Stable adsorption is a prerequisite for subsequent catalytic reactions. In the most 578 stable adsorption structure of FA (Figure S18), the O atom in FA bonds to the Pt atom while the carbon 579 atom in FA bonds with the Ti atom (corresponding to electronegativity values of 1.54 and 2.28 for Ti 580 and Pt, respectively). The C=O bond in FA undergoes an 18% activation (from 1.213 to 1.434 Å before 581 and after adsorption, respectively) due to the synergistic effect of Ti and Pt atoms. In contrast, the C=O 582 bond may not be activated to such an extent on conventional Pt catalysts. These observations indicate 583 that Pt₃Ti can effectively activate a C=O bond in FA, which is crucial for understanding the catalytic 584 mechanism. 585

The O_2 dissociatively decomposed into two isolated O* species after structural optimization on the Pt₃Ti catalyst surface. This exothermic reaction had an energy of up to -5.28 eV, which indicates that O₂ in catalytic FA oxidation is the source of O*. Moreover, because two isolated O atoms are adsorbed directly to the top positions of the Pt and Ti atoms, these atoms are expected to be excellent sites for synergistic catalysis. First-principle calculations show that H₂O, HCOO⁻, DOM, and CO can be stably present during catalytic FA oxidation to comply with the experimental results (Figure S18).

Table 5 shows the reactions involved in the catalytic FA oxidation process and the corresponding reaction-energy changes, indicating that all intermediate steps are exothermic and can proceed spontaneously. Figure S18 depicts the top view of the FA oxidation reaction proceeding on the 595 structured, dense stacking model. Figure 10 shows the side view of the FA oxidation reaction 596 proceeding on the structured ball-and-stick model. Almost all intermediates prefer to adsorb at the 597 bridge sites of Ti and Pt atoms, which indicates the presence of two simultaneous active sites during 598 catalytic FA oxidation.

For a more in-depth understanding of FA adsorption on the Pt₃Ti surface and the activation 599 mechanism and the deeper adsorption mechanism of DOM, HCOO⁻, and CO, we investigated the 600 601 electronic structure of the corresponding structures (Figures S19 and S20). The projected density of states for adsorbed FA shows strong hybridization between the FA 2p orbital and the Pt 3d and Ti 3d 602 orbitals near the Fermi level, indicating effective activation of the FA molecule. In contrast, the strong 603 adsorption of FA on the Pt₃Ti intermediate surface shifts its overall electronic state to a lower energy 604 level. The adsorption state therefore becomes stabilized, which is conducive to subsequent catalytic 605 reactions on the Pt₃Ti surface. The DFT simulation also demonstrated that H₂O is stable on the catalyst 606 surface ($E_{ads} = -0.25$ eV with a distance of 3.397 Å) because it is weakly adsorbed and does not occupy 607 activation sites. The theoretical simulations eliminate the possibility of hydrolysis, with no significant 608 changes in molecular configuration. The H₂O is therefore not a catalytic reactant, and the presence of 609 water vapor does not lead to a decrease in the activity of the catalyst, as demonstrated experimentally. 610

611 As for the activation mechanism of FA, the e⁻ distribution of gaseous FA molecules at the Fermi energy level moves to both sides of the Fermi energy level upon interaction with Pt and Ti atoms 612 (Figure S19a). FA coupling with the Pt 3d orbitals observed at lower Fermi energy levels (-4 to 0 eV) 613 indicates strong hybridization, and FA coupling with the Ti 3d orbitals was also observed at higher 614 Fermi energy levels (0 to 3.5 eV). The charge difference density (Figure S20a) shows an increase in 615 charge density between Ti and carbon atoms after FA adsorption, corresponding to enhanced 616 adsorption. Detailed adsorption and activation mechanisms of DOM, HCOO⁻, and CO can be 617 explained similarly (Figures S19 and S20). 618

619 The possible reaction pathways with a density generalized function approach from *O + *HCHO to *CO₂ + *H₂O products were studied subsequently. Possible routes for various products were 620 considered in the DFT calculations to determine the reaction network for FA oxidation on the Pt₃Ti 621 surface. The most probable reaction path is $*O + *HCHO \rightarrow *CH_2O_2 + *O \rightarrow *HCOO + *OH \rightarrow *CO$ 622 + 2 *OH \rightarrow *CO₂ + 2 *OH (Figure 11). According to the calculated thermodynamics data, DOM, 623 HCOO⁻, and CO intermediates were most easily generated during FA oxidation. The decomposition 624 625 of *HCOO to *CO and *OH was highly favored based on thermodynamic considerations. The reaction network in Figure 11 shows that, upon the activation of the C=O bond in FA, the O* generated by O₂ 626 cleavage further reacts with the carbon atom in FA to form an *H₂CO₂ intermediate. The catalytic 627 process from FA to *HCOO is exothermic and is, therefore, a downhill reaction. Experimental 628 evidence and DFT analysis also indicate that *HCOO is unstable and quickly decomposes into *CO + 629 *OH (Figure 11). The spontaneous decomposition of *HCOO to *CO + *OH gives way to a reaction 630 between *CO and O* to form CO₂. The presence of *OH in this reaction suggests a two-by-two process 631 encompassing the removal of an H₂O molecule and the formation of new O* species to participate 632 further in the catalytic FA oxidation process. 633

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635 4. FA removal performance comparison

As the basic means to assess the removal performance of a catalytic system, the reaction kinetic 636 rate (r) was a key metric. The relative removal performance of FA at RT conditions was compared 637 between the catalysts explored here (e.g., 0.1%, 1%, and 2% Pt/Ti₃C₂-R) and comparable catalysts 638 reported previously [7, 67, 68] (Table 6). According to this comparison, a tungsten-doped amorphous 639 iron oxide (FeO_x)-supported Pt catalyst (1.5%-Pt/a-FeW_{0.08}O_x) was the most effective performer for 640 FA removal, with an r value of 0.29 mol g⁻¹ h⁻¹ [69] (Table 6). For other catalysts, the r values ranged 641 from 0.0001 to 0.15 mol g⁻¹ h⁻¹, with the lower and upper extremes achieved by lanthanum (La)-doped 642 TiO₂ and iron(II,III) oxide (Fe₃O₄)-supported Pt catalysts, respectively [70, 71] (Table 6). 643

From an economic perspective, r values can be used to assess the actual performance of a catalyst 644 if they are normalized to the loaded content of the noble metal in association with the number of the 645 active sites [72]. In this regard, the activated carbon-supported Na-Pt catalyst (2% Na-0.2% Pt/AC) 646 was the more effective performer, as measured by the normalized r value of 0.61 mol g^{-1} h⁻¹ for Pt 647 (wt.%)⁻¹ [13] (Table 6). The 0.1% Pt/Ti₃C₂-R used in this study was the second most effective, with a 648 normalized r value of 0.55 mol g⁻¹ h⁻¹ for Pt (wt.%)⁻¹ (Table 6). Except for those two top performers, 649 the normalized r values fell in the range of 0.0002 to 0.22 mol g⁻¹ h⁻¹ for Pt (wt.%)⁻¹, corresponding to 650 the La/TiO₂ and manganese (Mn)/alkali titanate nanotube-supported Pt catalysts, respectively (Table 651 6). The normalized r value of 2% Na-0.2% Pt/AC (Na used as a promoter alongside Pt) was 1.1 times 652 higher than that of 0.1% Pt/Ti₃C₂-R. The Pt/Ti₃C₂ catalyst may therefore be regarded as a reasonably 653 competitive catalyst for FA oxidation at RT [13] (Table 6). As 0.1% Pt/Ti₃C₂-R contains only half of 654 655 the noble-metal content of 2% Na-0.2% Pt/AC, the former is more economically viable from the perspective of Pt loading [13] (Table 6). As the other catalysts may not effectively decompose FA 656 under humid conditions, the practicality of Pt/Ti₃C₂-R is even more pronouncing. 657

The r value can also be used to calculate the turnover frequency (TOF), which allows the potential utility of catalysts to be compared among each other in terms of the activity per site, although the concentration of active sites must be quantified. Because this can be challenging, we assumed that the concentration of available surface O* species represents the concentration of active sites [46]. Conversion of the r value into a TOF can be made using Equation 5.

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$$TOF\left(\frac{m \ m \ b_{FA}}{m \ d_O s}\right) = \frac{r\left(\frac{m \ d_{FA}}{g_{cat} h}\right) \times 10^6}{C_O\left(\frac{m \ d_O}{kg_{cat}}\right) \times 3,600 \ (\frac{s}{h})}$$
(5)

664 Only the reducible species below 350°C are considered here as they are inactive at elevated 665 temperatures due to requirements for a higher activation energy. The TOF can be calculated using Equation 6, with ξ representing the fraction of the total reduction signal below 350°C. A reasonable range of the TOF values can be calculated by evaluating the C₀ using the CO and H₂-TPR results.

$$668 \quad TOF = \frac{5r}{18C_0\xi} \tag{6}$$

Values for the TOF are listed in Table 7. The obtained TOF values are between 16.5 and 82.4 669 mmol_{FA} mol_O⁻¹ s⁻¹, an order of magnitude greater than those previously reported for total oxidation 670 [46, 73]. These results strongly support the outstanding catalytic performance of the catalysts 671 demonstrated in the present study. The TOF of the 2% Pt/Ti₃C₂ catalyst was the highest (82.4 ± 3.0 672 $\text{mmol}_{\text{FA}} \text{mol}_{\text{O}}^{-1} \text{ s}^{-1}$), although it maintained the lowest reaction rate (0.020 $\text{mol}_{\text{FA}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$). This can be 673 attributed to the small fraction of peaks (ξ) below 350°C (0.272 for the specific CO-TPR, compared 674 with values between 0.841 and 0.915 for all others). When only the H_2 -TPR results are used to 675 calculated TOF, the order is: 2% Pt/Ti₃C₂-R (60.1 ± 0.5) > 1%-Pt/Ti₃C₂-R (40.8 ± 0.4) > 2% Pt/Ti₃C₂ 676 (16.5 ± 2.3), with all TOF values expressed in $\text{mmol}_{\text{FA}} \text{mol}_{\text{O}}^{-1} \text{ s}^{-1}$. We therefore concluded that the 2% 677 Pt/Ti₃C₂-R catalyst achieved the highest TOF against FA oxidation. 678

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680 5. Conclusions

In this research, the superiority of 2D Ti₃C₂ MXene was demonstrated as a non-oxide support to 681 modulate active Pt sites in the catalytic oxidation of FA under dark conditions at RT. The RMSI 682 between Ti₃C₂ and Pt NPs helped achieve an X_{FA} to CO₂ conversion rate by forming a Pt₃Ti IMC via 683 reduction pre-treatment. The r value (mol g⁻¹ h⁻¹) for the RT FA oxidation reaction at a GHSV of 684 23,885 h⁻¹ (m_{cat} of 20 mg and F_{FA} of 3.4E-09 mol s⁻¹) increased in the following order: 2% Pt/Ti₃C₂ 685 (0.02) < 0.1% Pt/Ti₃C₂-R (0.054) < 1%-Pt/Ti₃C₂-R (0.058) < 2% Pt/Ti₃C₂-R (0.061). The 2% Pt/Ti₃C₂-686 R achieved a TOF of approximately 60 mmol_{FA} mol₀⁻¹ s⁻¹. The X_{FA} was lower with decreases in m_{cat} 687 or with increases in FA concentrations and flow rates. Remarkably, 100% XFA at RT was maintained 688

689	for 2% Pt/Ti ₃ C ₂ -R in the 0%–90% RH range for as long as 50 h (the maximum tested TOS). Analysis
690	of in situ DRIFTS indicated that FA oxidation on Pt/Ti ₃ C ₂ -R involves various intermediates (e.g.,
691	DOM. HCOO ⁻ , and CO). The DFT simulations elucidated the FA reaction mechanism, RMSI, and the
692	associated surface phenomena. According to detailed evaluation of performance, in terms of the
693	normalized r values, 0.1% Pt/Ti ₃ C ₂ -R, including 0.55 mol g^{-1} h ⁻¹ of Pt (wt.%) ⁻¹ , is one of the more
694	effective supported Pt catalysts ever reported for the FA oxidation reaction at RT under dark conditions.
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706	Data Availability Statement
707	The data will be made available subject to a reasonable request.
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Tables and Figures

Order	Material	BET surface terial area		BJH adsorption average pore diameter (4V/A)	Actual content (wt.%) ^b	
		$m^2 g^{-1}$	cm ³ g ⁻¹	nm	Pt	
1	Ti ₃ C ₂	6.7	0.012	4.9	_	
2	0.1% Pt/Ti ₃ C ₂	4	0.006	3.8	0.13	
3	1%-Pt/Ti ₃ C ₂	3.7	0.005	3.7	0.96	
4	2% Pt/Ti ₃ C ₂	3.3	0.004	3.4	2.1	
5	2% Pt/Ti ₃ C ₂ -R	19.8	0.023	3.5	_	

Table 1. Physical properties of Ti_3C_2 and Pt/Ti_3C_2 catalysts.

^a BJH adsorption cumulative volume of pores between 0.1 nm and 300 nm diameter.

^b Determined by ICP-OES.

Order	Sample	$C_0 (mol_0 kg_{cat}^{-1})$	T ₁	T ₂	T ₃	T ₄	T ₅	T ₆
1	Carrier (CO)	$(0.44 \pm 0.50) \times 10^{-2}$	191.6 ± 4.7	209.0 ± 1.3	250.5 ± 0.1	269.3 ± 0.3	306.9 ± 0.4	338.2 ± 0.1
1	i Carrier (CO)	$(9.44 \pm 0.30) \times 10$	(1.9 ± 0.4)	(3.4 ± 0.3)	(14.0 ± 1.0)	(38.8 ± 1.8)	(39.4 ± 1.1)	(2.5 ± 0.2)
2	2 2% Pt/Ti ₃ C ₂ (CO)	$(2.48 \pm 0.00) \times 10^{-1}$	187.4 ± 0.2	207.6 ± 0.4	283.6 ± 0.2	312.6 ± 0.3	491.8 ± 1.0	444.6 ± 0.7
2		$(2.48 \pm 0.09) \times 10$	(7.6 ± 0.1)	(1.1 ± 0.1)	(17.5 ± 0.2)	(1.0 ± 0.1)	(21.9 ± 1.3)	(50.9 ± 1.3)
3	2% Pt/Ti ₋ C ₋ -R (CO)	$(4.49 \pm 0.70) \times 10^{-1}$	217.6 ± 8.4	253.1 ± 2.8	285.1 ± 2.8	318.5 ± 0.6	491.9 ± 1.0	515.0 ± 0.3
5	$5 2701011_3 C_2^{-1} (CO)$	$(4.49 \pm 0.70) \times 10$	(20.7 ± 7.5)	(40.2 ± 15.5)	(29.8 ± 8.9)	(0.7 ± 0.2)	(6.4 ± 0.3)	(2.1 ± 0.3)
4	Carrier (H ₂)	$(1.04 \pm 0.21) \times 10^{-1}$	269.5 ± 1.0	258.1 ± 10.5	303.8 ± 3.9	431.5 ± 4.7	496.9 ± 1.4	553.0 ± 2.1
-		$(1.04 \pm 0.21) \times 10$	(2.3 ± 1.1)	(11.0 ± 3.8)	(4.6 ± 2.7)	(12.0 ± 4.6)	(57.0 ± 9.9)	(13.1 ± 5.4)
5	2% Pt/Ti _a C ₂ (H ₂)	$(4.05 \pm 0.11) \times 10^{-1}$	85.8 ± 1.8	125.6 ± 0.6	195.1 ± 0.3	271.6 ± 0.4	411.1 ± 0.8	481.3 ± 1.0
5	_/01011302(112)	$(4.05 \pm 0.11) \times 10$	(5.9 ± 0.5)	(9.3 ± 0.6)	(47.3 ± 0.7)	(20.7 ± 0.5)	(3.6 ± 0.3)	(13.3 ± 0.3)
6	2% Pt/Ti ₂ C ₂ -R (H ₂)	$(3.35 \pm 0.27) 10^{-1}$	67.8 ± 1.2	122.6 ± 2.5	207.3 ± 2.5	276.8 ± 1.1	419.0 ± 1.0	482.6 ± 2.0
	2.0101130210(112)	(3.35 ± 0.27) 10	(1.6 ± 0.3)	(13.5 ± 2.7)	(39.6 ± 6.5)	(29.4 ± 4.1)	(5.6 ± 0.5)	(10.3 ± 0.5)

991 brackets are the fractions of the total surface O* concentration (%).

Table 2. H_2 and CO-TPR results for the Ti_3C_2 carrier, 2% Pt/ Ti_3C_2 , and 2% Pt/ Ti_3C_2 -R catalysts. All temperatures are in °C and the values between

Order	Catalyst	Catalyst activation	T ₅₀ (°C) ^b	Т90 (°С) ^с	XFA (%) at 30°C	r (mol g ⁻¹ h ⁻¹) ^d			
1	2% Pt/Ti ₃ C ₂ -R		$< 30 (100\% X_{FA} at room temperature)$	$< 30 (100\% X_{FA} at room temperature)$	100	0.061			
2	1%-Pt/Ti ₃ C ₂ -R	Reduction at 300°C using $H_2 (10\%) + N_2$ mixture for 3 h (50 mL min ⁻¹)	$< 30 (94\% \ X_{FA}$ at room temperature)	< 30 (94% X _{FA} at room temperature)	94	0.058			
3	0.1% Pt/Ti ₃ C ₂ -R		< 30 (89% X _{FA} at room temperature)	33	89	0.054			
4	2% Pt/Ti ₃ C ₂	Heating at 300°C using N_2 for 3 h (50 mL min ⁻¹)	73	143	32	0.020			
^a Reacta	^a Reactant composition: FA (100 ppm) + air (balance), flow rate: 50 mL min ⁻¹ (3.4E-09 mol s ⁻¹), m_{cat} : 20 mg, and GHSV: 23,885 h ⁻¹ .								

994 **Table 3.** FA removal performance of the Pt/Ti_3C_2 catalysts.^a

 $^{\rm b}$ Reaction temperature corresponding to X_{FA} of 50%.

 $^{\rm c}$ Reaction temperature corresponding to X_{FA} of 90%.

^d Reaction rate obtained at 30°C.

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Table 4. Intermediate species (X) adsorbed on the Pt₃Ti surface during the catalytic oxidation of FA to CO₂ and H₂O and the corresponding adsorption energies (E_{ads}). E_{ads} of less than -0.5 eV can be considered chemisorption, with the mean intermediates stable on the catalyst surface. The shortest adsorption distance between the intermediate and catalytic active site is represented as D_m (all distances in Å). The Hirshfeld charge obtained from the surface of the catalyst Pt₃Ti-X during the adsorption process is described as ΔQ (e⁻). The adsorption site of X, the bond length of the intermediate in its free state (BL1 in Å), the target bond length after activation by the catalyst (BL2 in Å), and the activation ratio of the bond length (BL in %) are also provided.

Order	Х	E _{ads} (eV)	D _m (Å)	ΔQ (e ⁻)	Site	BL1 (Å)	BL2 (Å)	BL (%)	
1	НСНО	-1.72	2.04	-0.25	Br _{Ti-Pt}	1.434	1.213	18	-
2	O ₂	-5.28	1.619	-0.41	TTi and TPt	2.881	1.222	136	
3	H_2O	-0.25	3.397	0.1	Br _{Pt-Pt}	1.006	0.975	3	
4	0	-8.10	1.703	-0.27	$\mathrm{Br}_{\mathrm{Ti-Pt}}$	-	_	-	
5	HCOO	-5.27	1.835	-0.2	Br _{Ti-Pt}	1.211	1.263	-4	
6	H_2CO_2	-6.91	1.758	-0.27	Br _{Ti-Pt}	1.38	1.396	-1	
7	СО	-2.85	2.213	-0.12	Br_{Ti-Pt}	1.174	1.138	3	
8	CO ₂	-2.56	2.123	-0.48	$\mathrm{Br}_{\mathrm{Ti-Pt}}$	1.305	1.172	11	

Order	Elementary reaction	ΔH (eV)
1	*HCHO + O* \rightarrow *H ₂ CO ₂	-7.68
2	$*H_2CO_2 + O* \rightarrow *HCOO + *OH$	-3.08
3	*HCOO + O* \rightarrow *CO ₂ + *OH	-2.66
4	*HCOO \rightarrow *CO + *OH	-2.16
5	$*CO + O* \rightarrow *CO_2$	-6.61
6	$O_2 + * \rightarrow *O + *O$	-5.28
7	$*OH + *OH \rightarrow *H_2O + *O$	-4.37

Table 5. The energies (Δ H in eV) of the reactions involved in the FA oxidation process.

	Pt (wt.%)	m _{cat} (mg)	Catalyst activation	Reactant composition	FA concentration (ppm)	Flow rate (mL min ⁻¹)	F _{FA} (mol s ⁻¹)	Space velocity	X _{FA} (%) at 30°C	r (mol g _{cat} ⁻¹ h ⁻¹) ^a	No (n (P
AC	0.2	30	$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{l} FA + O_2 \ (20 \ vol.\%) \ + \\ RH \ (35\%) \ + \ He \\ (balance) \end{array}$	150	100	1.0E-08	80,000 h ⁻¹	100	0.12	0.0
	0.5	100	Reduction at 400°C using H_2 for 3 h (100 mL min ⁻¹)	$FA + O_2 (20 \text{ vol.\%}) + N_2 (balance)$	500	100	3.4E-08	70,000 h ⁻¹	89	0.11	0.2
₀₈ O _x	1.5	10	-	FA + RH (50%) + air (balance)	120	100	8.2E-09	600,000 mL $h^{-1} g^{-1}$	100	0.29	0.2
	0.8	50	$\begin{array}{llllllllllllllllllllllllllllllllllll$	FA + air (balance)	100	500	3.4E-08	600,000 mL h ⁻¹ g ⁻¹	60	0.15	0.3
	0.6	250	$\begin{array}{ll} \mbox{Reduction} & \mbox{at} \\ \mbox{300°C using } H_2 \mbox{ at} \\ \mbox{150 mL min}^{-1} \end{array}$	$FA + O_2 (22 \text{ vol.\%}) + N_2 (balance)$	81.4	1,200	6.7E-08	300,000 mL h ⁻¹ g ⁻¹	40	0.04	0.0
ГіO ₂	0.08	100	$\begin{array}{llllllllllllllllllllllllllllllllllll$	FA + RH (50%) + air (balance)	10	170	1.2E-09	100,000 mL h ⁻¹ g ⁻¹	80	0.003	0.0
iNT	0.2	200	$\begin{array}{llllllllllllllllllllllllllllllllllll$	FA + RH (35%) + air (balance)	50	100	3.4E-09	30,000 mL h ⁻¹ g ⁻¹	100	0.006	0.0
	2	200	$\begin{array}{llllllllllllllllllllllllllllllllllll$	$FA + O_2$ (20%) + Ar (balance)	100	200	1.4E-08	50,000 h ⁻¹	93	0.02	0.0
	0.5	500	$\begin{array}{llllllllllllllllllllllllllllllllllll$	FA + RH (50%) + Air (balance)	10	1,000	6.8E-09	120,000 mL h ⁻¹ g ⁻¹	98	0.005	0.0
	0.5	2,800	$\begin{array}{llllllllllllllllllllllllllllllllllll$	FA + Air (balance)	61	800	3.3E-08	8,000 h ⁻¹	100	0.004	0.0
	1	500	Reduction at 400°C using H ₂ (mixed with Ar) for 4 h	FA + RH (50%) + air (balance)	10	1,000	6.8E-09	120,000 mL h ⁻¹ g ⁻¹	100	0.005	0.0
	1	60	Reduction during the synthesis process through the addition of NaBH ₄	$FA + O_2 (20 \text{ vol.\%}) + N_2 (balance)$	20	50	6.8E-10	50,000 mL h ⁻¹ g ⁻¹	100	0.004	0.0
TiO ₂	0.5	100	-	$FA + O_2 (21\%) + RH$ (50%) + N ₂ (balance)	0.5	100	3.4E-11	60,000 mL h ⁻¹ g ⁻¹	98	0.0001	0.0
	0.1	20	Reduction at 300°C using 10 vol.% H ₂ (mixed with N ₂) for 3 h	FA + air (balance)	100	50	3.4E-09	23,885 h ⁻¹	89	0.05	0.:

val performance of supported Pt catalysts in a continuous mode of operation.

1009 Table 7. TOF of the tested catalysts (FA oxidation was evaluated at RT with a GHSV of

1010 23,885 h⁻¹). ξ is the fraction of the TPR signal for T < 350°C.

Order	Catalyst	$C_O (mol_O kg_{cat}^{-1})$	$r (\text{mol}_{FA}\text{g}_{cat}^{-1}\text{h}^{-1})$	ξ	TOF (mmol _{FA} mol ₀ ⁻¹ s ⁻¹)
1	2% Pt/Ti ₃ C ₂	$(2.48 \pm 0.09) 10^{-1}$ (CO-TPR)	0.020	0.272	82.4 ± 3.0
		$(4.05 \pm 0.57) 10^{-1} (\text{H}_2\text{-TPR})$		0.831	16.5 ± 2.3
2	1%-Pt/Ti ₃ C ₂ -R	$(4.44 \pm 0.04) 10^{-1} (H_2-TPR)$	0.058	0.889	40.8 ± 0.4
		$(4.84 \pm 0.03) 10^{-1} (\text{CO-TPR})$		0.909	36.6 ± 0.2
3	2% Pt/Ti ₃ C ₂ -R	$(3.35 \pm 0.03) 10^{-1} (H_2-TPR)$	0.061	0.841	60.1 ± 0.5
		$(4.49 \pm 0.07) 10^{-1} (\text{CO-TPR})$		0.915	41.2 ± 0.6
1011					
1012					
1013					
1014					



Figure 1. Physicochemical characterization results. (a) PXRD pattern for Ti₃C₂, 0.1% Pt/Ti₃C₂,
1%-Pt/Ti₃C₂, and 2% Pt/Ti₃C₂. (b) PXRD pattern of 2% Pt/Ti₃C₂-R. (c) TGA profiles of Ti₃C₂,
0.1% Pt/Ti₃C₂, 1%-Pt/Ti₃C₂, and 2% Pt/Ti₃C₂. (d) N₂ adsorption-desorption isotherms of Ti₃C₂,
0.1% Pt/Ti₃C₂, 1%-Pt/Ti₃C₂, 2% Pt/Ti₃C₂, and 2% Pt/Ti₃C₂-R. The closed and open symbols
represent adsorption and desorption, respectively.



Figure 2. TPR profiles until 623 K using CO (a, b, c) and H_2 (d, e, f) with a heating rate of 10 K min⁻¹ (Gaussian model). (-) peak 1, (-) peak 2, (-) peak 3, (-) peak 4, (-) peak 5, (-) peak 6, and (-) total calculated signal.



Figure 3. TPR data analysis. (a) Peak temperatures for 2% Pt/Ti₃C₂-R versus 2% Pt/Ti₃C₂; \diamond denotes CO-TPR data and \circ denotes H₂-TPR data. Peak temperature for 2% Pt/Ti₃C₂ (blue symbol) and 2% Pt/Ti₃C₂-R (red symbol) versus carrier material in (b) CO-TPR and (c) H₂-TPR.



Figure 4. Deconvoluted Ti 2p XPS spectra of the analyzed materials. (a) Ti₃C₂. (b) 0.1% Pt/Ti₃C₂.

1089 (c) 1%-Pt/Ti₃C₂. (d) 2% Pt/Ti₃C₂. Note that the black line indicates the raw data.



Figure 5. Deconvoluted Pt 4f XPS spectra of the analyzed catalysts. (a) 0.1% Pt/Ti₃C₂. (b) 1%Pt/Ti₃C₂. (c) 2% Pt/Ti₃C₂. Note that the black line indicates the raw data.





Figure 7. FA removal performance of the Pt/Ti₃C₂ catalysts. (a) Light-off curve (FA concentration: 1147 100 ppm in air, catalyst mass = 20 mg, flow rate = 50 mL min⁻¹, and RH = 0%). (b) Effect of 1148 catalyst bed mass (catalyst: 2% Pt/Ti₃C₂-R, FA concentration = 100 ppm in air, catalyst mass = 5-1149 20 mg, flow rate = 50 mL min⁻¹, and RH = 0%). (c) Effect of flow rate (catalyst: 2% Pt/Ti₃C₂-R, 1150 FA concentration = 100 ppm in air, catalyst mass = 20 mg, flow rate: 50-250 mL min⁻¹, and RH 1151 = 0%). (d) Effect of FA concentration (catalyst: 2% Pt/Ti_3C_2 -R, FA concentration = 100–735 ppm 1152 in air, catalyst mass = 20 mg, flow rate = 50 mL min^{-1} , and RH = 0%). (e) Effect of RH (catalyst: 1153 1154 2% Pt/Ti₃C₂-R, FA concentration = 100 ppm in air, catalyst mass = 20 mg, flow rate = 50 mL min⁻ 1155 ¹, and RH =0%–90%). (f) Time-on-stream performance of 2% Pt/Ti₃C₂-R catalyst (FA concentration: 100 ppm in air, catalyst mass = 150 mg, flow rate = 25 mL min^{-1} , and RH = 0%). 1156





Figure 9. Schematic of the optimized Pt_3Ti structure to study the FA oxidation mechanism. (a) Top view of Pt_3Ti ball-stick model. (b) Side view of Pt_3Ti ball-stick model. (c) Schematic of the catalytic FA oxidation reaction with the participation of O_2 . (d) Top view of Pt_3Ti closely packed model. (e) Side view of Pt_3Ti closely packed model. The red letters in panels (a) and (d) indicate the types of metal atoms. The part of the structure dotted in green represents the specific hexacoordinate structure of Pt_3Ti . Blue and gray spheres represent Pt and Ti atoms, respectively.

- 1192
- 1193
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- 1195
- 1196
- 1197
- 1198



Figure 10. Side view of critical structures in catalytic FA oxidation on a Pt₃Ti surface (bridge site

1211 between Ti and Pt atoms).



Figure 11. Thermodynamics of FA oxidation on a Pt₃Ti surface. (a) Free-energy diagram for *O₂
decomposition into two O* species. (b) The optimal (red) and secondary (blue) reaction pathways

1227 for the oxidation of FA into CO_2 and H_2O under the action of O^* .