

On the reduction of CO₂ footprint via selective hydrodeoxygenation by ZnO-Ti₃C₂T_x catalyst under solvent-free conditions

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Biomass-derived fatty acids are essential feedstock for producing liquid fuels and value-added chemicals with significantly low CO₂ footprints. Herein, Ti₃C₂T_x and ZnO-Ti₃C₂T_x catalysts were synthesized and demonstrated for selective hydrodeoxygenation reaction (HDO) of methyl oleate (MO) as the model compound. The synthesized ZnO-Ti₃C₂T_x catalyst showed 100% conversion of MO with >90% selectivity for HDO product (n-C18). Additionally, the pure Ti₃C₂T_x demonstrated 100% conversion with a selectivity of 67% for n-C17 hydrocarbon via the decarboxylation route. The highest reduction of CO₂ footprint is achieved at 280°C and 30 bar H₂ pressure under solvent-free conditions using ZnO-Ti₃C₂T_x. The catalyst is recyclable and reusable after five test cycles. The high catalytic selectivity of the ZnO-Ti₃C₂T_x catalyst towards HDO is attributed to the synergic effect of Ti and ZnO active sites with a robust and thermally stable structure. The study offers an efficient route for converting edible and non-edible vegetable oils to biofuels by controlling CO₂ production.

4.1 Experimental section

4.1.1 Synthesis of Ti₃C₂T_x and ZnO-Ti₃C₂T_x composite

Ti₃C₂T_x was prepared by etching of Al from the MAX (Ti₃AlC₂) phase precursor. Ti₃C₂ solution was prepared by slowly immersing 2g MAX power in 40 mL, an aqueous solution of 40 wt.% HF acid with the addition of a magnetic stir bar in a polypropylene beaker and continuously stirred at room temperature for 24 hr as reported in our previous study.[44] The resultant solution of Ti₃C₂T_x is centrifuged at 4000 rpm and washed out several times with DI water to remove AlF₃ and excess HF acid till the pH of the solution nearly reaches 7. To obtain Ti₃C₂T_x flakes, the solution was dispersed in 150 ml water and sonicated for 3 hours to increase the layers' interspacing. Further filtration was finally dried in a vacuum oven at 80°C to obtain multilayer Ti₃C₂T_x.

ZnO-Ti₃C₂T_x was prepared by a one-pot hydrothermal process. First, 200mg Ti₃C₂T_x was dispersed in water and sonicated for 20 minutes to obtain a homogenous suspension, followed by adding 0.5 M zinc acetate and 0.25M of NaOH solution under stirring to get a white suspension. Finally, the white solution was mixed with Ti₃C₂ solution and added to 33mL of DI water to synthesize 5, 10, and 15 wt.% ZnO into Ti₃C₂T_x named MXZ-5 MXZ-10, and MXZ-15, respectively. The resulting mixture was subjected to hydrothermal reaction at 180°C for 12hr. The obtained product was washed several times to remove unreacted precursor and dried at 60°C for overnight in a vacuum oven. Afterward, the samples were calcinated at 400°C in an N₂ atmosphere.

4.1.2 Hydroprocessing of methyl oleate

The prepared catalyst (5 mg–30 mg), methyl oleate (100 µL), and 25 mL of n-heptane were filled in a stainless-steel container (supplied by Amar Equipments Pvt. Ltd.) to proceed with the hydrotreatment reaction. Initially, the vessel was purged with hydrogen gas thrice to remove atmospheric gases and the desired pressure for the hydrogenation reaction was maintained. The reaction temperature was slowly increased from room temperature with a ramp of 10°C/min and maintained for experimental hours to achieve the required temperature. After the completion of the reaction, the reaction mixture was allowed to cool down to 35°C under ambient conditions. The n-heptane solution was added to the reaction mixture and centrifuged to extract the product. Further, the product was analyzed by gas chromatography. Based on the peak area of obtained

saturated hydrocarbon, the relative quantity of products was estimated using internal software of gas chromatography. The gas chromatograph techniques were used to calculate the conversion of methyl oleate as well as the selectivity of C17 and C18 by the eqs. (1), (2) and (3).

$$\text{conversion} = \frac{\text{mol}_{\text{initial reactant}} - \text{mol}_{\text{unreacted reactant}}}{\text{mol}_{\text{initial reactant}}} \times 100 \quad (1)$$

$$\text{Selectivity of C17} = \frac{\text{mol}_{\text{C17}}}{\text{mol}_{\text{products}}} \times 100\% \quad (2)$$

$$\text{Selectivity of C18} = \frac{\text{mol}_{\text{C18}}}{\text{mol}_{\text{products}}} \times 100\% \quad (3)$$

To determine the total liquid fraction by considering unreacted methyl oleate and hydrotreated products, the obtained liquid fraction was weighed. Liquid and gas fraction can be calculated by eqs. (4) and (5), respectively.

$$\text{Liquid fraction} = \frac{\text{weight of liquid product}}{\text{weight of feed}} \times 100\% \quad (4)$$

$$\text{gas fraction} = 1 - \frac{\text{weight of liquid product}}{\text{weight of feed}} \times 100\% \quad (5)$$

4.2 Results and discussion

4.2.1 Characterization of catalyst

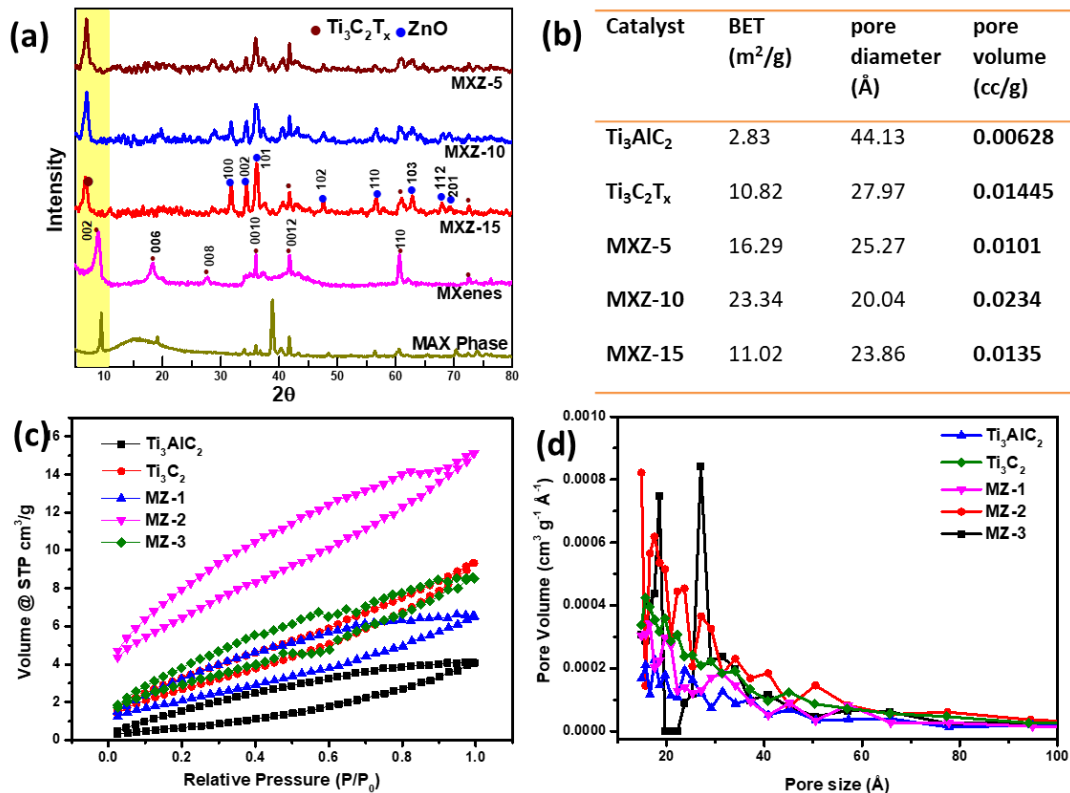


Figure 4.1 (a) XRD patterns, (b) BET surface area analysis and porosity parameter, (c) N₂ adsorption-desorption isotherms (d) and pore size distribution of Ti₃AlC₂, Ti₃C₂T_x, and ZnO-Ti₃C₂T_x nanocomposites (MXZ-5, MXZ-10 and MXZ-15).

Figure 4.1 a shows the X-ray diffraction patterns of Ti_3AlC_2 , $\text{Ti}_3\text{C}_2\text{T}_x$, and various $\text{Ti}_3\text{C}_2\text{-ZnO}$ composites. $\text{Ti}_3\text{C}_2\text{-ZnO}$ composites were synthesized with different wt% loading of ZnO with 5%, 10%, and 15% and named MXZ-5, MXZ-10, and MXZ-15, respectively. XRD pattern for the composites indicates the hexagonal wurtzite crystal structure of ZnO with the P63mc space group (JCPDF No 036-1451). The well-defined diffraction peaks observed at 2θ values of 9.5° , 19.1° , 33.9° , 36.0° , 38.7° , 41.7° , 48.4° , 56.4° , 60.5° , 65.5° , 70.3° , and 74° are indexed to the (002), (004), (100), (103), (104), (105), (107), (109), (110), (1011), (2021) and (2024) planes, respectively for the Ti_3AlC_2 crystal phase (JCPDS 52-0875). The maximum intense peak at 39° corresponds to the (104) plane, which is diminished for $\text{Ti}_3\text{C}_2\text{T}_x$, which confirms the removal of the Al layer from the Ti_3AlC_2 . [46] After exfoliation, the 002 peaks of Ti_3AlC_2 were shifted toward a lower angle, indicating a decrease in interlayer bonding and the c-lattice parameter (Naguib et al., 2011). The diffraction peaks of $\text{Ti}_3\text{C}_2\text{T}_x$ at 9° , 18.4° , 27.8° , and 60.7° can be indexed corresponding to the (002), (006), (008) and (110) planes, respectively. Additionally, the peak observed at 36.1° , and 41.8° correspond to (0010) and (0012), indicating the peaks of the TiC and TiO_2 . This may be due to the oxidation of $\text{Ti}_3\text{C}_2\text{T}_x$ during etching processes (Soomro et al., 2021). XRD pattern of $\text{Ti}_3\text{C}_2\text{T}_x$ -ZnO composites contain ZnO and $\text{Ti}_3\text{C}_2\text{T}_x$ peaks, indicating the successful incorporation of hexagonal wurtzite ZnO. As synthesized $\text{Ti}_3\text{C}_2\text{T}_x$ -ZnO composites showing a characteristic peak at 31.6° , 34.4° , 36.3° , 47.6° , 56.6° , 62.8° , 67.9° , and 69.4° were assigned to the (100), (002), (101), (102), (110), (103), (112) and (201) planes, respectively. A further shift of the (002) plane towards the lower angle indicates the larger interlayer spacing and successful incorporation of ZnO.

Nitrogen adsorption-desorption isotherms of Ti_3AlC_2 , $\text{Ti}_3\text{C}_2\text{T}_x$, and ZnO- $\text{Ti}_3\text{C}_2\text{T}_x$ composites were used to find the specific surface areas and pore size distribution and are shown in Figure 4.1 c. The Brunauer-Emmett-Teller (BET) surface area of Ti_3AlC_2 , $\text{Ti}_3\text{C}_2\text{T}_x$, and MXZ-5, MXZ-10, and MXZ-15 obtained are 2.83, 10.82, 16.29, 23.34, and $11.02 \text{ m}^2\text{g}^{-1}$, respectively. The increased surface area of ZnO- $\text{Ti}_3\text{C}_2\text{T}_x$ composites is due to the occurrence of ZnO particles between the interlayer spacing of $\text{Ti}_3\text{C}_2\text{T}_x$. The large surface area has more significant advantages in improving the catalyst efficiency for biofuel production. (Bharti et al., 2019) The surface area of MXZ-15 decreased compared to MXZ-5 and MXZ-10, possibly, due to aggregation of ZnO particles at higher loading of ZnO. As can be observed (Figure 4.1 d), all samples have pore volumes ranging from 0.0062 to 0.0234 cc/g . The obtained average BJH pore diameter was 20–45 Å, as shown in Table 1. It can be inferred that mesoporosity could provide a way to load more significant active sites to guest molecules, boosting HDO reaction.

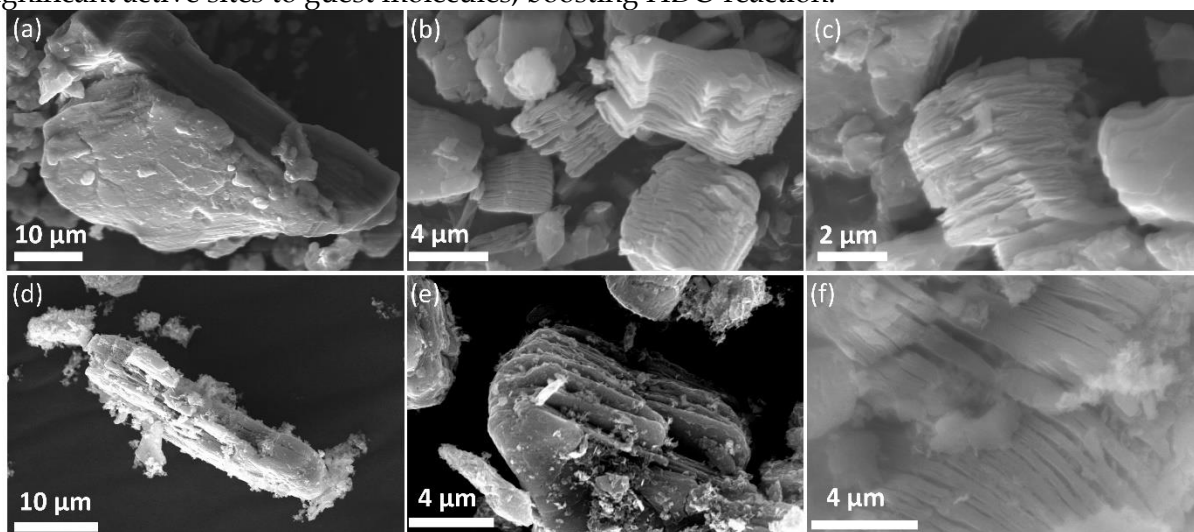


Figure 4.2. SEM image of Ti_3AlC_2 (a), $\text{Ti}_3\text{C}_2\text{T}_x$ (b,c) and ZnO- $\text{Ti}_3\text{C}_2\text{T}_x$ nanocomposites (d, e and f).

The SEM image of the MAX and $\text{Ti}_3\text{C}_2\text{T}_x$ is shown in **Figure 4.2 (a and b-c)**, respectively. From **Figure 4.2 (a)**, it can be deduced that the MAX phase does not have a layer structure. After the HF acid treatment, a layered $\text{Ti}_3\text{C}_2\text{T}_x$ structure was obtained. **Figure 4.2 (b and c)** show the morphological features of the $\text{Ti}_3\text{C}_2\text{T}_x$ layered structure with different magnification ranges. From the SEM images, the thickness of the layered structure $\text{Ti}_3\text{C}_2\text{T}_x$ varies from 2 nm to 10 nm,

which predominantly depends upon delaminating agents and etching reaction time. **Figure 4.2 (d-f)** shows the different composite of ZnO- $\text{Ti}_3\text{C}_2\text{T}_x$ with variable wt% of ZnO. The SEM image and EDS elemental mapping of pristine ZnO show the nanoflakes structure and elements distribution in **Figure 4.4**. The elemental composition and distribution of the elements Ti, Zn, C, O, F, and Al in multilayered ZnO- $\text{Ti}_3\text{C}_2\text{T}_x$ composites were confirmed by EDS (**Figure 4.3**).

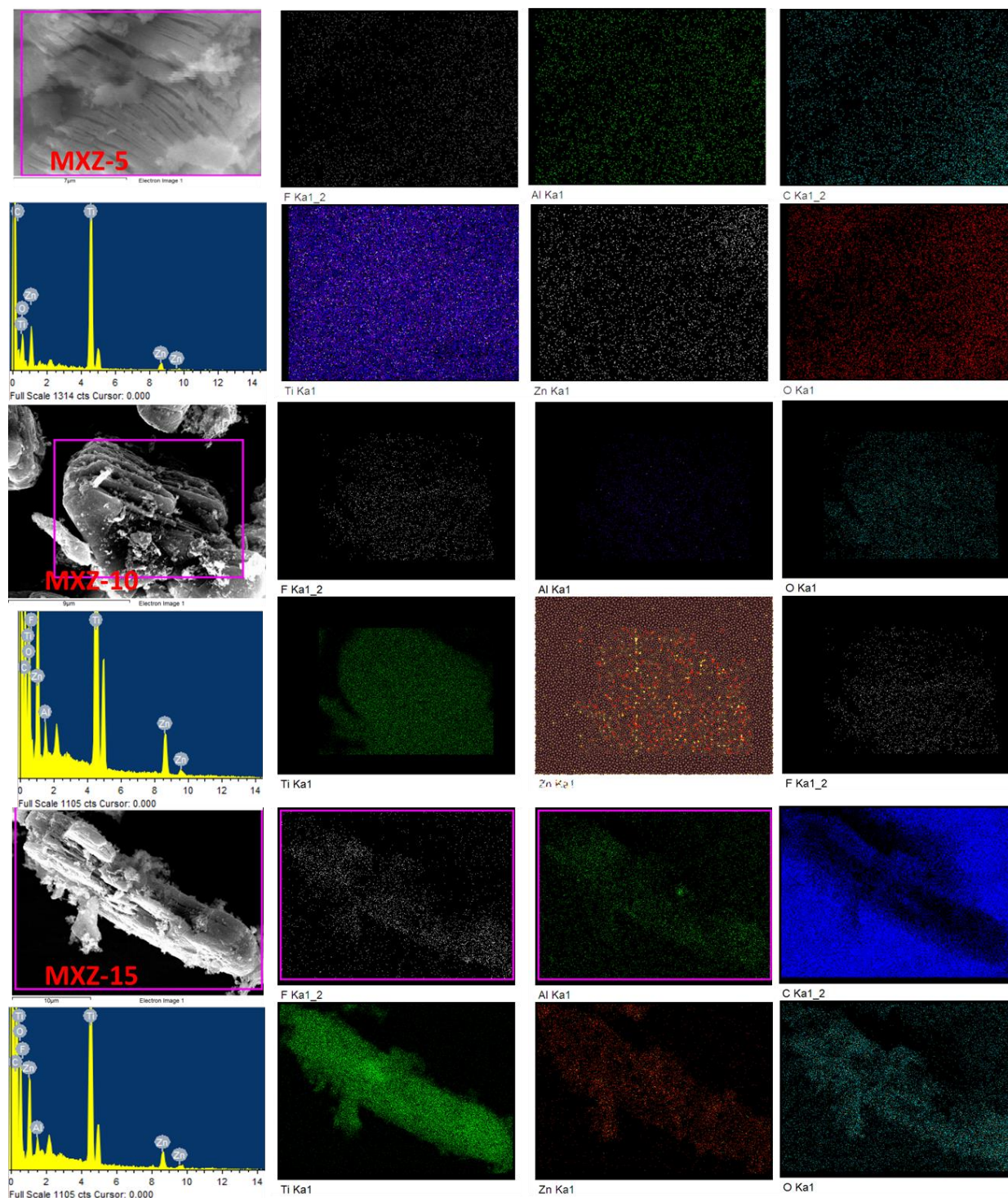


Figure 4.3: SEM image and EDX elemental mapping of MXZ-5, MXZ-10 and MXZ-15.

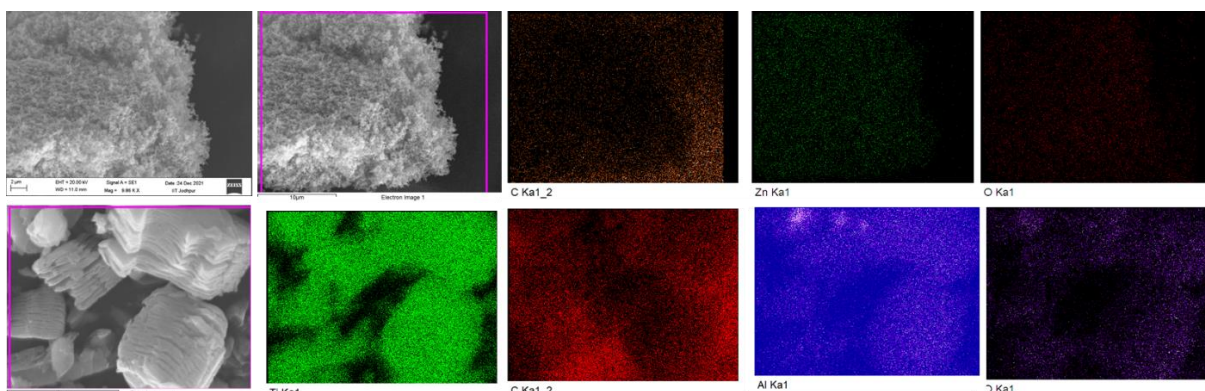


Figure 4.4: SEM image and EDX elemental mapping of pristine ZnO and MXene.

The less intense peaks obtained for Al signifies the replacement of Al from Ti_3AlC_2 along with the surface group like O and OH. The element O is observed in EDX due to the formation of ZnO, TiO_2 , and surface termination group with F, OH, and O. The F signatures in EDX are observed because of surface fluoride attaches to Ti during HF treatment.

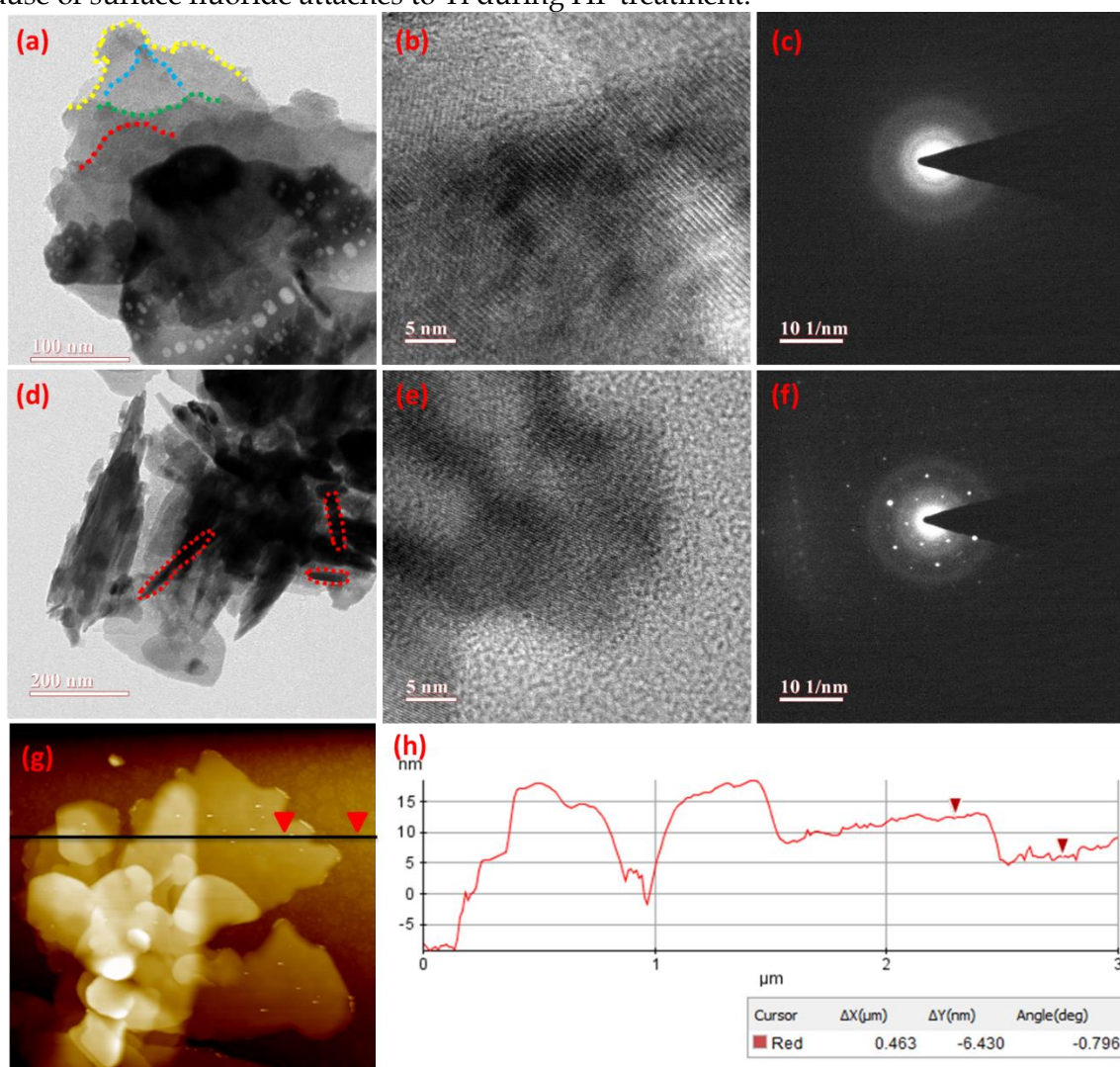


Figure 4.5 Low and high magnified TEM image of $\text{Ti}_3\text{C}_2\text{Tx}$ (a, b), $\text{ZnO-Ti}_3\text{C}_2\text{Tx}$ nanocomposites (d, e) and corresponding SAED pattern (c and f); AFM image of $\text{Ti}_3\text{C}_2\text{Tx}$ (g) and its height profile (h).

The TEM image of the delaminated $\text{Ti}_3\text{C}_2\text{Tx}$ and $\text{ZnO-Ti}_3\text{C}_2\text{Tx}$ are shown in **Figure 4.5**. The $\text{Ti}_3\text{C}_2\text{Tx}$ layer is very thin and transparent, as shown in **Figure 4.5** (a). The dotted lines indicate that the $\text{Ti}_3\text{C}_2\text{Tx}$ layers overlap each other. Fig 4 b clearly shows the interlayer spacing of 0.98 nm corresponding to the (002) plane of $\text{Ti}_3\text{C}_2\text{Tx}$. Figure 4 (d-f) indicates the $\text{ZnO-Ti}_3\text{C}_2\text{Tx}$ composites and the corresponding SAED pattern. The red dotted line represents the rice-like

nanostructured ZnO visible in Figure 4.5 d. The SAED pattern of ZnO-Ti₃C₂T_x composites shows the hexagonal symmetry that confirms the wurtzite ZnO. **Figure 4.5 (g and h)** shows the AFM image of the exfoliated Ti₃C₂T_x and its corresponding height measurement. It can be noted that the delaminated Ti₃C₂T_x layered shows a thickness of 6.4 nm due to the overlapped layer structure. **Figure 4.5 g** reveals the multilayer topology of the Ti₃C₂T_x.

The temperature-programmed desorption (TPD) measurements were carried out in the temperature range of 100-900°C to understand NH₃ desorption and acid sites on the surfaces of Ti₃C₂T_x, and ZnO-Ti₃C₂T_x, and the results are shown in **Figure 4.6**. After one-hour pre-treatment at 200°C (10°C/min) in He, the NH₃ adsorption was performed at 100°C for 1 h. The chemisorption peaks of the Ti₃C₂T_x catalyst can be classified into three sites: weak, medium and strong acidic sites. The peaks at 698, and 767°C are due to the presence of surface groups like O, -OH, and -F, which results in the strong chemisorption to NH₃. (Camiloti et al., 1999, Verma et al., 2017) The calculated acidic sites are 2.5 and 25.04 μmol due to medium and strong acidic sites, respectively. Additionally, a strong acidic site was observed at 610°C for the ZnO-Ti₃C₂T_x catalyst, due to the Zn metal of ZnO nanoflakes. (Ranaware et al., 2019) The increased acidic sites (3.3 μmol) at medium acidic sites influence the selectivity of the C17 and C18 hydrocarbons. The strong acidic site (24.95) for the ZnO-Ti₃C₂T_x catalyst also shifted toward the lower temperature site due to the additional peak of ZnO.

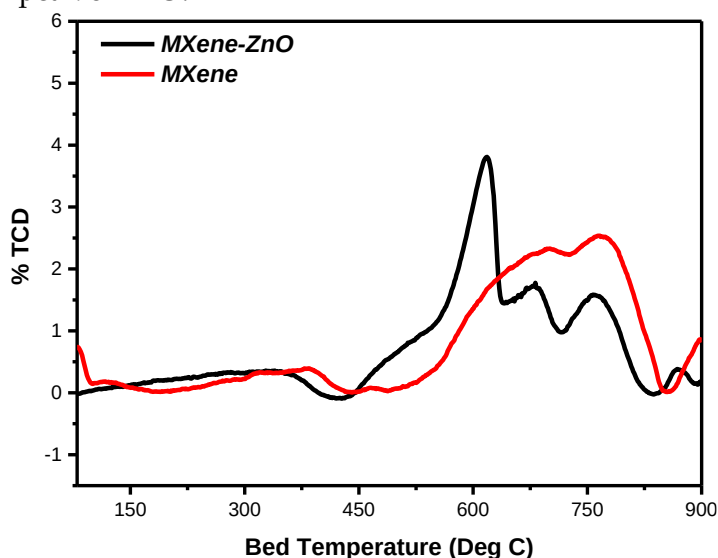


Figure 4.6 NH₃ TPD spectra of Ti₃C₂T_x, and ZnO-Ti₃C₂T_x nanocomposite.

The chemical composition and electronic state of different elements in ZnO-Ti₃C₂T_x composites were analyzed by XPS characterization. Fig. 5a shows survey spectra of the ZnO-Ti₃C₂T_x composite, which confirm the presence of Ti 2p, Zn 2p, C 1s, O1s, and F 1s. Fig. 5(b to f) reveals the high-resolution spectra of individual elements of Ti 2p, O1s, Zn 2p, C1s, and F 1s. In Ti 2p core level spectra (Fig. 5b), the peaks centered at 459.1 and 464.8eV correspond to Ti-O 2p_{3/2} and Ti-O 2p_{1/2} bond. (Goyal et al., 2011, Xia et al., 2017) Other peaks at 455.3 and 462.8eV are related to the Ti-C-Tx 2p_{3/2} and T-C-Tx 2p_{1/2}. The peaks at 459.1eV, ascribing to Ti-O 2p_{3/2} imply the partial oxidation of Ti₃C₂T_x into TiO₂. The O1s spectrum is fitted with two doublets centered at 530.6 and 532.3 eV corresponding to the TiO₂ and Ti-OH group, which further confirms the oxidation of Ti₃C₂T_x. (Epling et al., 1996) In Fig. 5d, The Zn 2p spectrum was fitted into two peak segments located at 1022 and 1045.1 eV, denoted to Zn 2p_{3/2} and Zn 2p_{1/2}, respectively. The High-resolution C1s spectrum shown in Fig. 5e was fitted into three peak sections situated at 381.5, 284.8, and 289.3 eV, attributed to Ti-C, C-C, and C-O, respectively. (Liu et al., 2018a) In the F 1s spectrum, the peaks observed at 684.9 and 685.9eV, correspond to Ti-F and Al-F, which confirms the presence of the F terminated group on the surface of Ti₃C₂T_x caused by HF etching. (Cao et al., 2017b)

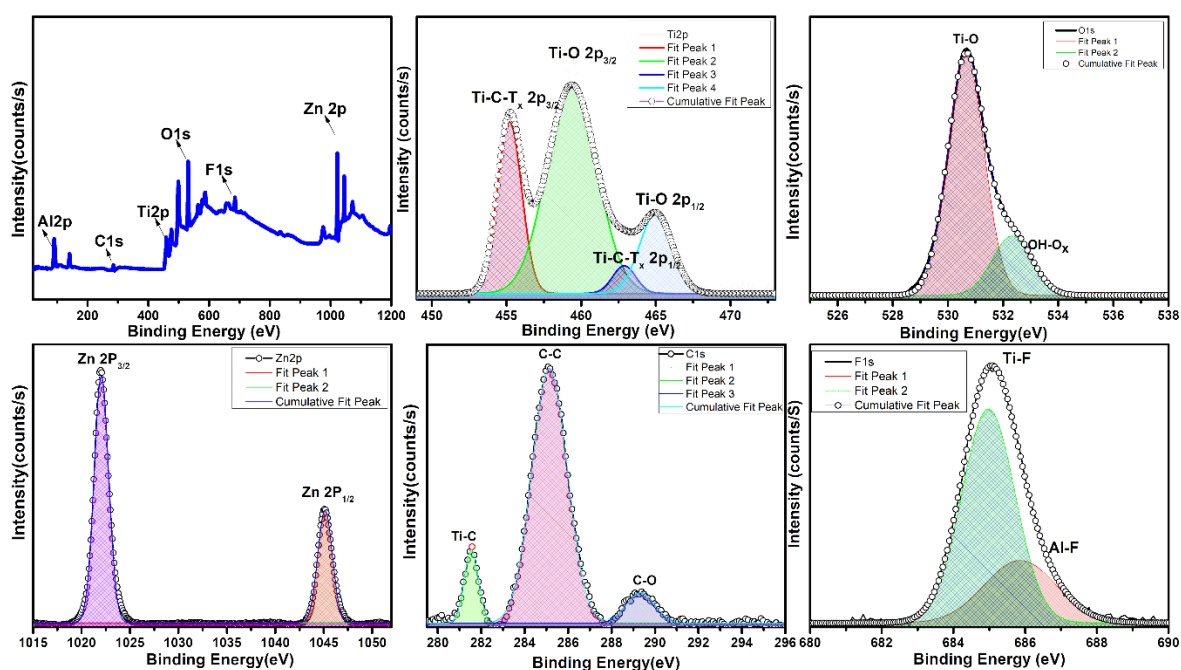


Figure 4.7. XPS spectra of ZnO-Ti₃C₂T_x nanocomposites: (a) Survey spectra, high resolution spectra of (b) Ti 2p, (c) O 1s, (d) Zn 2p, (e) C 1s and (f) F 1s.

4.2.2 HDO reaction of Pristine Ti₃C₂T_x

Table 4.1. Hydrotreatment results of methyl oleate with Ti₃C₂T_x catalyst at different temperature (200-320°C), pressure (15-20 bar) and time (08-15h).

Entry	Reaction	Temp.	P	Time	Solvent	Conversion	Selectivity (%)	
		(°C)					n-C17	n-C18
1.	MX-01	200	20	08	n-heptane	36.02±0.92	28.98±0.86	71.02±0.49
2.	MX-02	250	20	08	n-heptane	56.79±0.83	33.76±0.54	47±0.71
3.	MX-03	250	30	08	n-heptane	58.76±0.66	10.6±1.12	12.12±1.08
4.	MX-04	280	30	08	n-heptane	63.77±0.71	36.96±0.90	37.93±0.87
5.	MX-05	280	30	12	n-heptane	100±0	47.14±0.89	41.25±0.92
6.	MX-06	320	30	12	n-heptane	100±0	34.39±0.44	45.51±0.08
7.	MX-07	320	30	12	None	70.7±0.59	47.02±0.57	38.49±0.32
8.	MX-08	280	30	12	None	66.63±0.44	43±0.97	35.99±1.04
9.	MX-09	280	30	15	None	76.43±1.03	33.87±1.28	37.81±1.02
10.	MX-10	280	40	15	None	98±0.38	41.53±0.92	43.39±0.45
11.	MX-11	300	40	15	None	96±0.56	45.66±0.70	54.34±0.69
12.	MX-12	300	30	15	None	100±0	61.32±0.79	33.37±1.11
13.	MX-13	300	25	15	None	100±0	66.59±0.29	33.41±1.32
14.	MX-14	300	10	15	None	36.02±0.92	28.98±0.86	71.02±0.49

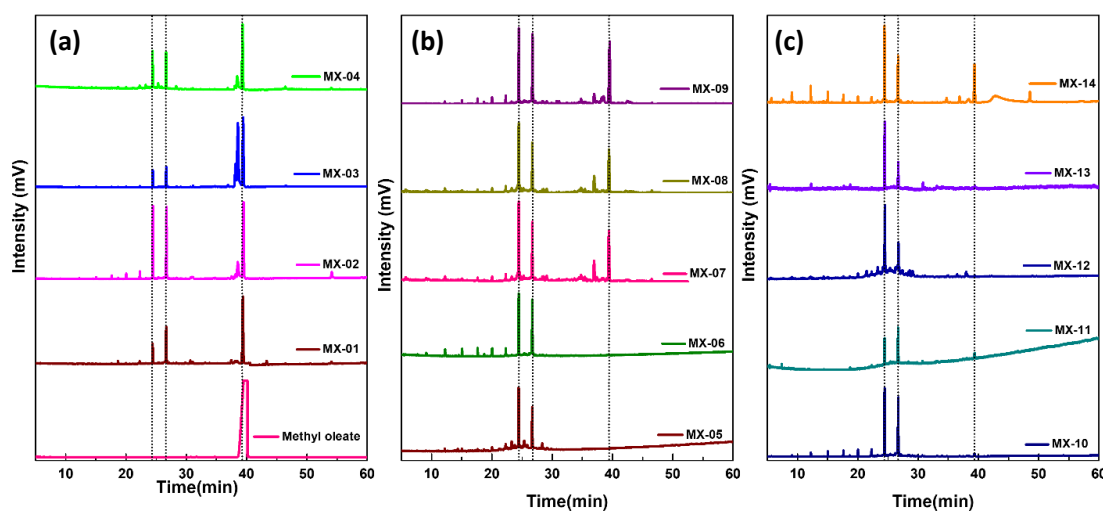


Figure 4.8. GC chromatogram of pure methyl oleate and for biodiesel product over $\text{Ti}_3\text{C}_2\text{T}_x$ catalyst, (a) pure methyl oleate and from MX-01 to MX-04, (b) MX-05 to MX-09, and (c) MX-10 to MX-14.

MXene catalyzed HDO of fatty acid-based biomass conversion and hydrogenation reactions got very few attentions. The ester group of MO model compound can be converted to diesel-range alkanes by decarboxylation/decarbonylation (DCX/DCN) to yield C17 alkane or by hydrodeoxygenation (HDO) to produce C18 alkane.[10] The catalytic processes were investigated at different temperatures, pressure, time, and catalyst loading conditions to identify the ideal condition to achieve selectivity for n-C18. The $\text{Ti}_3\text{C}_2\text{T}_x$ catalyst was mixed with MO, and the reactions were performed at a temperature range of 200 to 320°C. The obtained results were extracted from the GC and illustrated in **Figure 4.8** and **Table 4.1**. The catalytic reactions were also carried out in the presence and absence of solvent. All the reactions were performed with 20 mg catalyst and 100 μl MO. The experiments were carried out using $\text{Ti}_3\text{C}_2\text{T}_x$ catalyst and named as MX (01-14) where the numbers 01 to 14 denote the different experimental sets. The hydrotreatment reactions MX-01 to MX-14 (entry 1-14) were performed at different temperatures ranging from 200-320°C, at 10-40 bar pressure at different time intervals in the presence (n-heptane) and absence of solvent. All these reactions gave moderate (~36 %) to complete conversion of MO to lower n-alkanes with variable selectivity towards HDO. Poor conversion (36 to 64%) was obtained at a lower temperature (MX-01 to MX-04) even in n-heptane as solvent. The peak observed at 38.45 min is due to the intermediate products formed in between the reactions due to the partial hydrogenation of MO (MX-02), which increases with temperature (MX-03) due to favourable conditions for aldehyde and alcohol intermediates formation. When the temperature was raised to 280°C, higher conversion with competitive selectivity was observed for n-C17 and n-C18 along with lower hydrocarbons. The lower hydrocarbons are formed by cracking, as observed in the chromatogram at lower retention times than 24 min. The aggregation of smaller by-products formed during cracking suppresses the catalyst's active site, leading to poor conversion and selectivity (entry 1-4). (Cheng et al., 2017) Complete conversion and high selectivity of C17 and C18 were observed when the reaction time was increased to 12 h (entry 5). Further enhanced temperature has increased cracking products with marginal improvement in HDO selectivity (entry 6). The high conversion rate was obtained in n-heptane solvent as it promotes the MO conversion. (Deng et al., 2018) The solvent-free reactions have great economic and environmental advantages and are industrially viable. (Sinhamahapatra et al., 2010, Shim et al., 2018) Under a similar condition as reactions MX-06, MX-07 gave a lower conversion of 66.70 %. Usually, solvent-free reactions require higher temperatures to achieve complete conversion of methyl oleate to n-alkanes compared to reactions with solvents, as solvent plays a significant role in increasing the reaction rate. Lowering temperature from 320 to 280°C, compromised the conversion of MO as seen in entry 8 (MX-08). However, almost complete conversion (98%) was obtained in reaction MX-10 upon increasing hydrogen pressure and reaction time (280°C, 40 bar for 15 hr) provides high selectivity for n-C17 and n-C18.

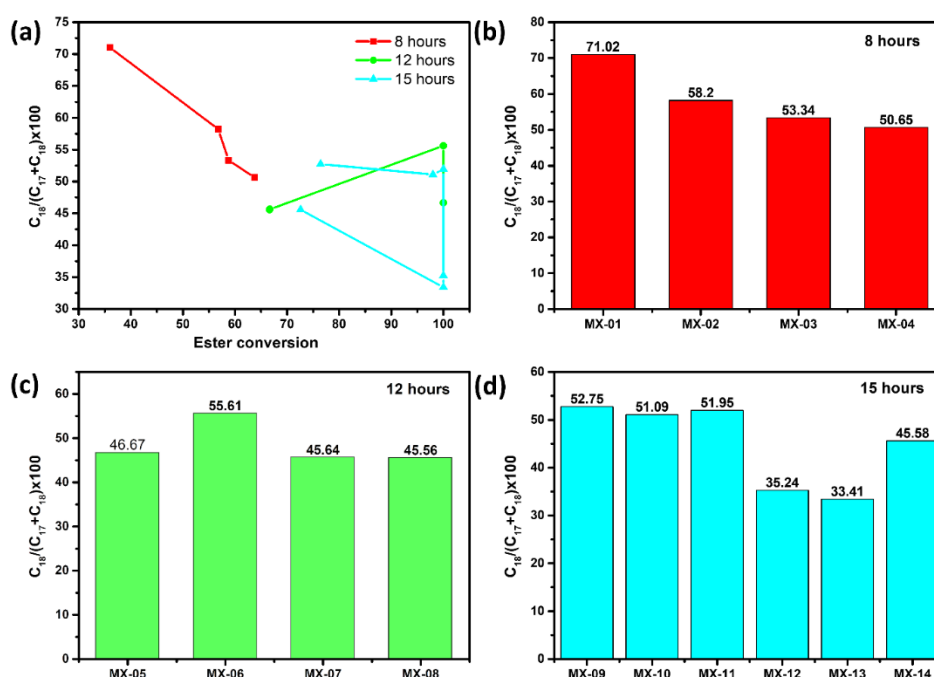


Figure 4.9. Variation in the selectivity of C18 vs % ester conversion at 8, 12, and 15 h (a) and bar diagram of C18 selectivity vs Ti_3C_2Tx catalyst (b, c, and d) at 8, 12, and 15 h.

Further, an increase in the temperature from 280°C to 300°C leads to full conversion of MO at 40 bar pressure for 15 h with higher selectivity of C18 (MX-11). The selectivity of n-C18 decreases when pressure decreases from 40 to 30 bar (MX-12) at 300°C for 15 h with observed selectivity of 61.32% for n-C17 and 33.37% for n-C18. Under the same reaction conditions at 25 bar, higher selectivity of n-C17 (66.59%) was observed (MX-13). Further reduction in pressure to 10 bar led to low conversion (72.60%) and low selectivity (MX-14). While using the pristine Ti_3C_2Tx catalyst, the variation in the selectivity of C18 (with respect to C17) vs ester conversion at 8 h, 12 h, and 15 h is shown in **Figure 4.9a**. According to the results, the selectivity of C18 decreases with an increase in reaction time, indicating that reactions with extended time provide lower hydrocarbon products. **Figure 4.9 (b, c, and d)** shows time-dependent conversion and C18 selectivity at 8 h, 12 h, and 15 h respectively.

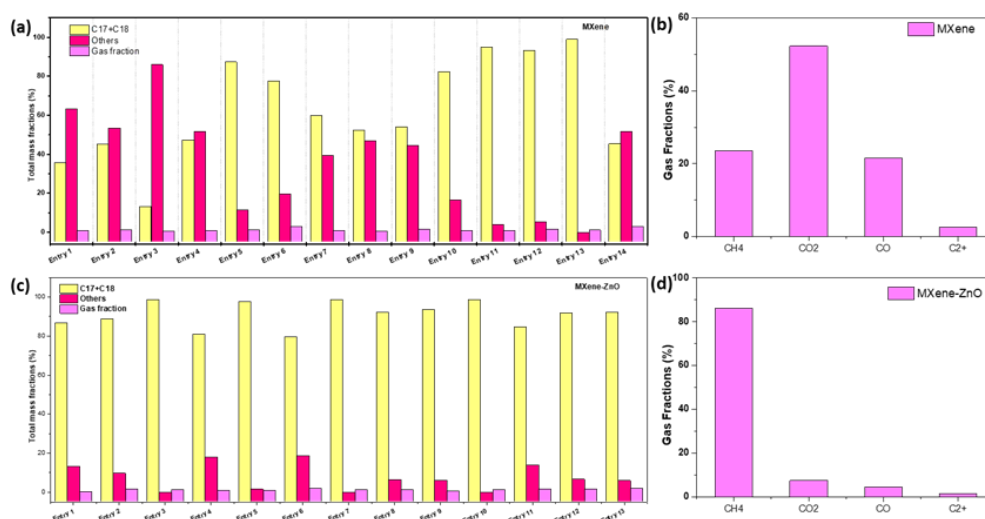


Figure 4.10: (a&c) The carbon balance for MXene and MXene-ZnO; (b) gas compositions using MXene catalyst (entry 13) and MXene-ZnO catalyst (entry 9).

The compositions of the gaseous products produced with different catalysts analyzed by GC-TCD is shown in Figure 4.10. The gas phase mainly comprised CH₄, CO₂, CO, C₂H₄, C₂H₆, and C₃H₈. The 86% of CH₄ observed in entry 13 generally originated from the demethylation of the methyl ester. In this reaction, the release of more C₂H₆ and C₃H₈ hydrocarbon gases might be

attributed to the further cleavage of alkyl groups in the oxygenated compounds during deoxygenation, decarbonylation, hydrodeoxygenation and decarboxylation of volatile vapor. As seen from Figure 4.10 (b), CO₂ is mainly a gas component from the decarboxylation of methyl oleate using a pristine MXene catalyst.

4.2.3 Selective HDO reaction of ZnO- Ti₃C₂T_x composites

Table 4.2. Hydrotreatment results of methyl oleate with ZnO-Ti₃C₂T_x catalyst (MXZ-5, MXZ-10, and MXZ-15) at different temperature (250-280°C), pressure (13-15 bar) and time (13-15h).

Entry	Reaction	Temperature	Pressure	Time	Conversion	Selectivity (%)	
		(°C)	(bar)	(h)	(%)	n-C17	n-C18
1.	MXZ-10 A	250	25	15	94.68±0.68	8.79±0.59	82.86±0.95
2.	MXZ-10 B	270	25	15	95.38±0.92	8.85±1.02	85.68±0.54
3.	MXZ-10 C	280	25	15	100±0	9.79±0.75	90.01±0.66
4.	MXZ-10 D	280	20	15	100±0	7.71±0.82	74.09±0.33
5.	MXZ-10 E	280	30	15	100±0	13.64±1.12	84.92±0.68
6.	MXZ-10 F	280	40	15	100±0	9.59±0.35	71.5±0.87
7.	MXZ-10 G	300	40	15	100±0	30.64±1.01	69.46±0.63
8.	MXZ-10 H	280	40	13	100±0	11.57±0.89	81.87±0.58
9.	MXZ-10 I	280	30	13	100±0	3.91±1.21	90.04±0.76
10.	MXZ-10 J	260	30	13	100±0	40.43±0.67	59.57±0.88
11.	MXZ-10 K	240	30	13	86±0.77	43.9±0.89	42.1±0.61
12.	MXZ-5 L	280	30	13	100±0	28.49±1.09	64.86±0.55
13.	MXZ-15 M	280	30	13	100±0	53.5±0.74	40.54±0.28

The catalytic reactions were performed with ZnO-Ti₃C₂T_x over MO under a temperature range of 250 to 300°C with variable pressure, reaction time, and catalyst loading. The associated GC results are shown in **Table 4.2** and **Figure 4.11**. The hydrotreatment reactions of ZnO-Ti₃C₂T_x catalyst are named as MXZ-10 (A-K), MXZ-5 L, and MXZ-15 M (here, MXZ-5 = 5% ZnO- Ti₃C₂T_x, MXZ-10 = 10% ZnO- Ti₃C₂T_x, MXZ-15 = 15% ZnO-Ti₃C₂T_x) and alphabets (A to M) represent the various experiments. Hydrogenation is the most crucial step in the formation of diesel grade fuel from the double bond containing methyl esters like methyl oleate (C₁₉H₃₄O₂), methyl linoleate (C₁₉H₃₄O₂), and methyl ricinoleate (C₁₉H₃₆O₃). In the case of methyl oleate, the double bond hydrogenation led to the formation of a methyl stearate radical, followed by H atom isomerization to give another alkyl radical. (Naik et al., 2011) However, removing the ester group from methyl oleate or triglycerides can reduce the O/C ratio effectively. ZnO catalyst works as basic and acidic by generating both acidic and basic sites. (Yadav et al., 2017) The incorporation of ZnO into Ti₃C₂ gave more selectivity towards n-C18 alkanes (Table 3) by increased acidic sites of the catalyst as confirmed by the NH₃ TPD. (**Figure 4.6**) It is also possible that ZnO incorporation forms zinc oleate and zinc carboxylates during the hydrogenolysis process of the catalyst, which improves the selectivity and rate of reaction compared to pristine Ti₃C₂T_x. (Reinoso et al., 2012, Reinoso et al., 2015) Here, the carbonyl lone-pairs interact with the Lewis acidic Zn²⁺, making it

more feasible for nucleophilic attack. (Chin et al., 2006) Furthermore, ZnO has a greater surface area to volume ratio, favouring effective recovery during the reusability test.

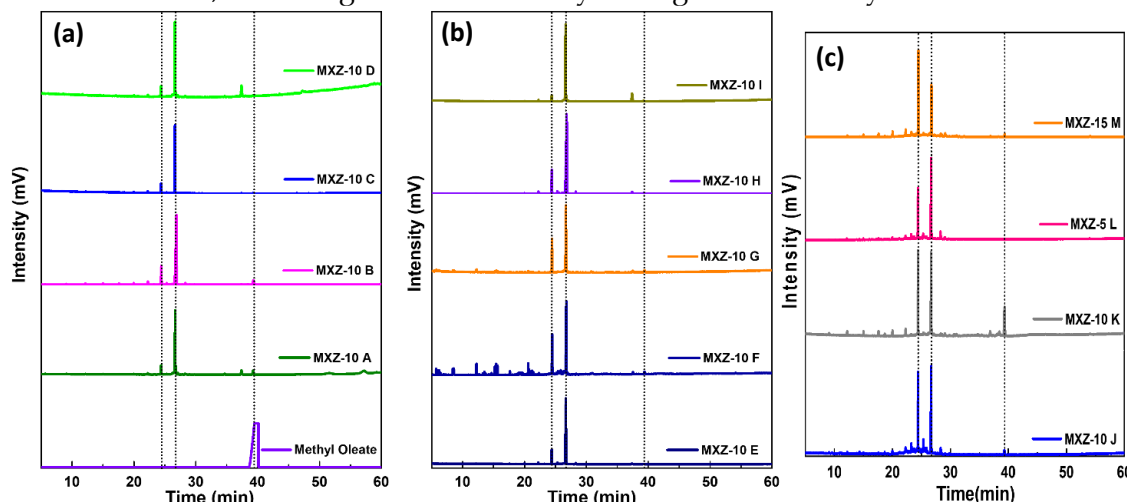


Figure 4.11. GC chromatogram of pure methyl over ZnO-Ti₃C₂T_x catalyst; (a) Pure Methyl Oleate and MXZ-10 A to MXZ-10D, (b) reactions from MXZ-10 to MXZ-10I, (c) reactions from MXZ-10J to MXZ-15 M.

During the reaction, the zinc oleate and zinc carboxylates could be a source of constant precursor supply for onsite catalyst formation. Interestingly, 94.68% conversion was seen even at 250°C and 25 bar pressure in 15 hours. (Table 4.2, reaction MXZ-10 A), which increased with temperature (reaction MXZ-10 B). The complete conversion was achieved at 280°C at variable pressure with good selectivity towards n-C18 (reactions MXZ-10 B to F). At high pressure (30 bar), the selectivity of n-18 increased to 84.92%, indicating high-pressure requirements for the higher selectivity of n-C17 and n-C18 (MXZ-10E). As expected, higher temperatures led to cracking products and compromised the alkane selectivity (reaction MXZ-10 G). Best selectivity (90.04%) for C18 was achieved under optimized conditions at 280°C, 30 bar for 13 h for C18 alkanes (MXZ-10 I). Low reaction temperature gives low selectivity (MXZ-10 J) and incomplete conversion (MXZ-10 K). Variation in the selectivity of C18 (with respect to C17) vs % conversion at 15 h and 13 h using catalyst MXZ-10 is shown in Figure 4.12 (a and b). Fig 4.12 (c) represents the catalytic activity of all three tested catalysts for HDO reaction. Out of three, MXZ-10 shows exceptional selectivity towards C18 and is effective towards CO₂ footprint reduction under optimized reaction conditions.

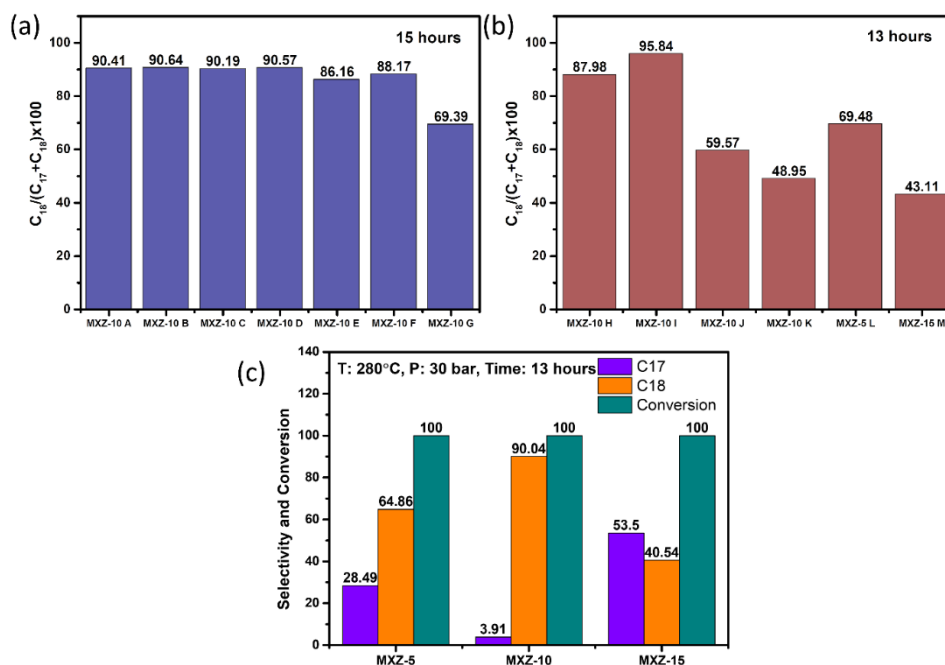


Figure 4.12. (a and b) Bar diagram of C18 selectivity vs ZnO-Ti₃C₂T_x catalysts at 15 and 13 h. (c) conversion and selectivity of various ZnO-Ti₃C₂T_x catalysts.

4.2.4 Selective HDO reaction with variable catalyst amount

Table 4.3. Hydrotreatment results of methyl oleate with Ti₃C₂T_x at 300°C, 25 bar and 15h (Entry 1-6).and ZnO-Ti₃C₂T_x catalyst (MXZ-10) at 280°C, with different weight loading at 300°C, 25 bar for 13h.

Entry	Catalyst	Temp (°C)	Pressure (bar)	Time (h)	Conversion (%)	Selectivity (%)	
						n-C17	n-C18
1.	MX 5mg	300	25	15	71	33.00	34.04
2.	MX 10mg	300	25	15	79	16.96	12.44
3.	MX 15mg	300	25	15	87	19.92	71.38
4.	MX 20mg	300	25	15	100	66.59	33.41
5.	MX 25mg	300	25	15	100	51.98	44.15
6.	MX 30mg	300	25	15	100	36.28	20.12
7.	MXZ-10 5mg	280	30	13	66	24.61	41.05
8.	MXZ-10 10mg	280	30	13	75.45	26.96	48.01
9.	MXZ-10 15mg	280	30	13	89	16.34	60.81
10.	MXZ-10 20mg	280	30	13	100	3.91	90.04
11.	MXZ-10 25mg	280	30	13	100	13.98	81.23
12.	MXZ-10 30mg	280	30	13	100	23.04	74.88

To understand the impact of catalyst loading, the hydrotreatment reactions of Ti₃C₂T_x and ZnO-Ti₃C₂T_x were investigated under optimized reaction conditions MX-13 and MXZ-10I, respectively, varying catalytic loading from 5mg to 30 mg (for 100 µL methyl oleate) as presented in **Table 4.3** and **Figure 4.13**. For Ti₃C₂T_x, hydrocarbon conversion increases with catalytic loading with complete conversion at 20mg (**Table 4.3**, entries 1-4). Undesirable products such as aldehyde and alcohols were formed at low catalytic loading, while higher loading promotes the cracking products (**Figure 4.13a**). For ZnO-Ti₃C₂T_x catalyst, amount variation (5mg to 30mg) provides incomplete conversion for lower catalyst loading and complete conversion for higher catalyst loading as shown in **Figure 4.13b** (**Table 4**, entries 7-9). Lowering catalytic loading under optimized conditions compromises the selectivity despite complete conversion (reactions MXZ-5 L and MXZ-15 M). Higher catalyst loading decreases the C18 selectivity (**Table 4**, entries 11 and 12). The relationship of selectivity to C18 vs % ester conversion at different weight % of Ti₃C₂T_x and ZnO- Ti₃C₂T_x catalyst is shown in **Figure 4.14**.

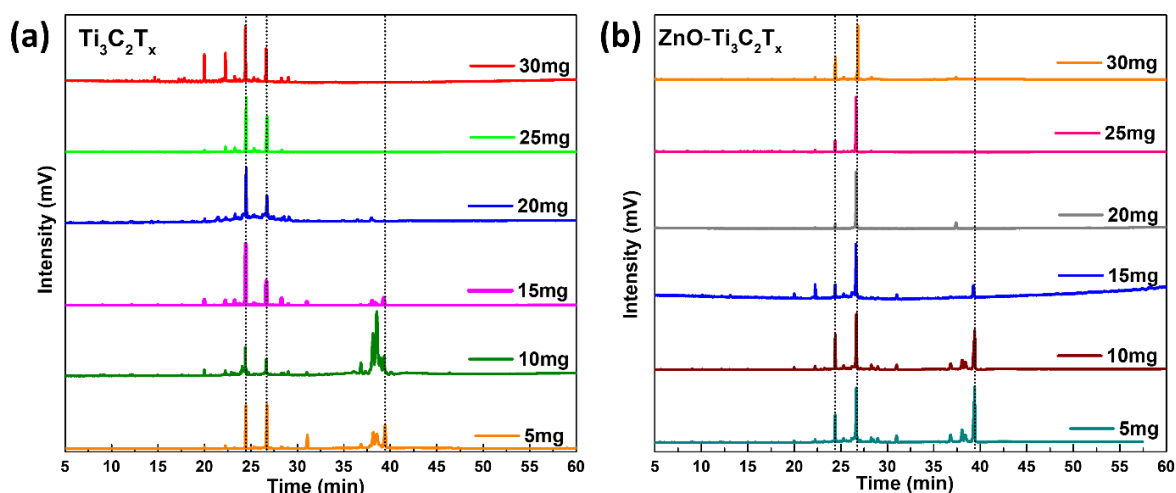


Figure 4.13. (a and b) GC chromatogram of $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{ZnO-Ti}_3\text{C}_2\text{T}_x$ with variable catalyst loading.

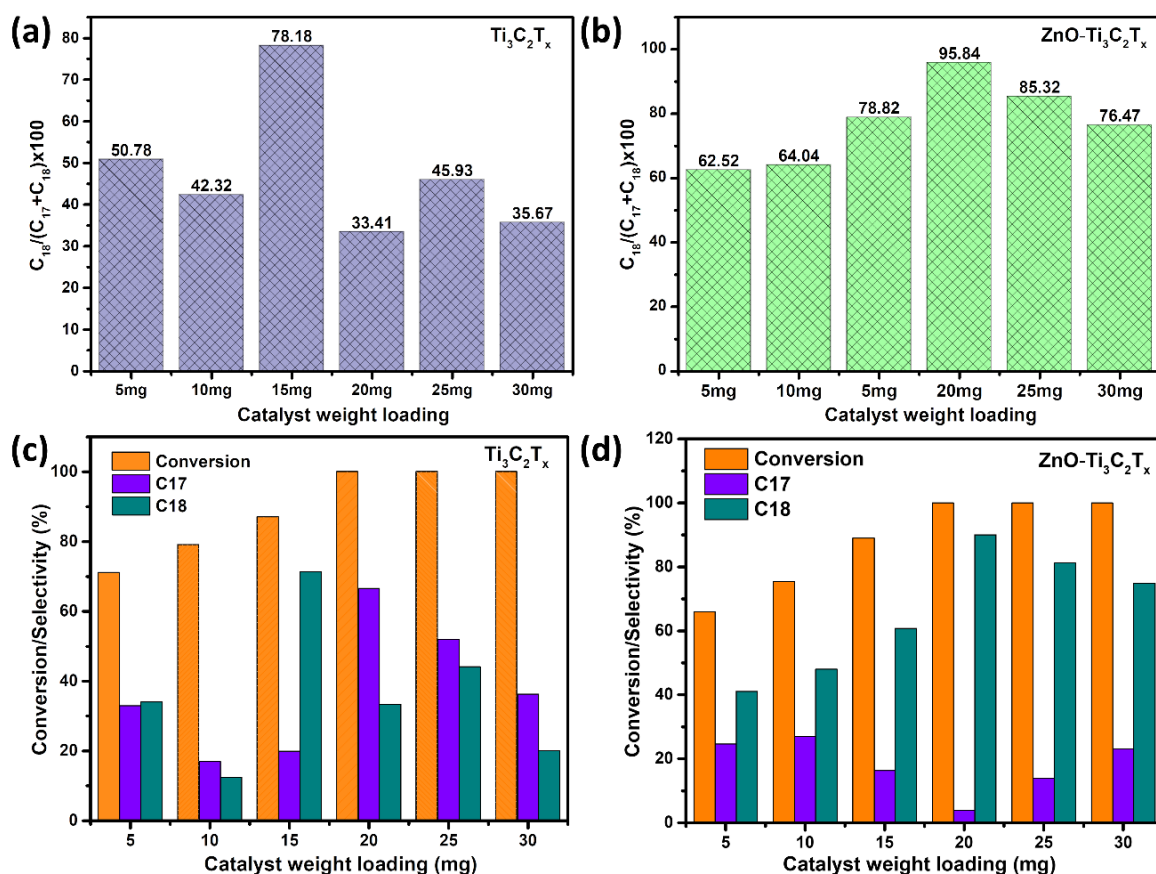


Figure 4.14. C18 selectivity vs $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{ZnO-Ti}_3\text{C}_2\text{T}_x$ catalysts with different catalyst weight loading (a and b); conversion and selectivity of $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{ZnO-Ti}_3\text{C}_2\text{T}_x$ with different catalyst weight loading (c and d).

4.2.5 Recyclability test of catalyst

The catalyst recyclability was tested under optimized reaction conditions for $\text{Ti}_3\text{C}_2\text{T}_x$ and MXZ-10 up to five cycles using 80mg catalyst, as represented in Figure 4.15 (a-b), respectively. The catalysts showed excellent recyclability without any significant drop in conversion, although selectivity was compromised with cycles. The spent catalyst was recovered (>95%) from the reaction vessel using n-heptane and dried at 100°C for 3 h in an argon atmosphere to prevent the $\text{Ti}_3\text{C}_2\text{T}_x$ oxidation and used for the next cycle. The XRD, SEM and EDX images of spent catalysts are shown in Figure 4.15 c-e. A slight drop in catalytic efficiency is due to its less delaminating structure. The XRD of the reused catalyst showed only slight changes in intensity, revealing that the MXZ-10 catalyst is stable and highly active even after 5 cycles and can be used further.

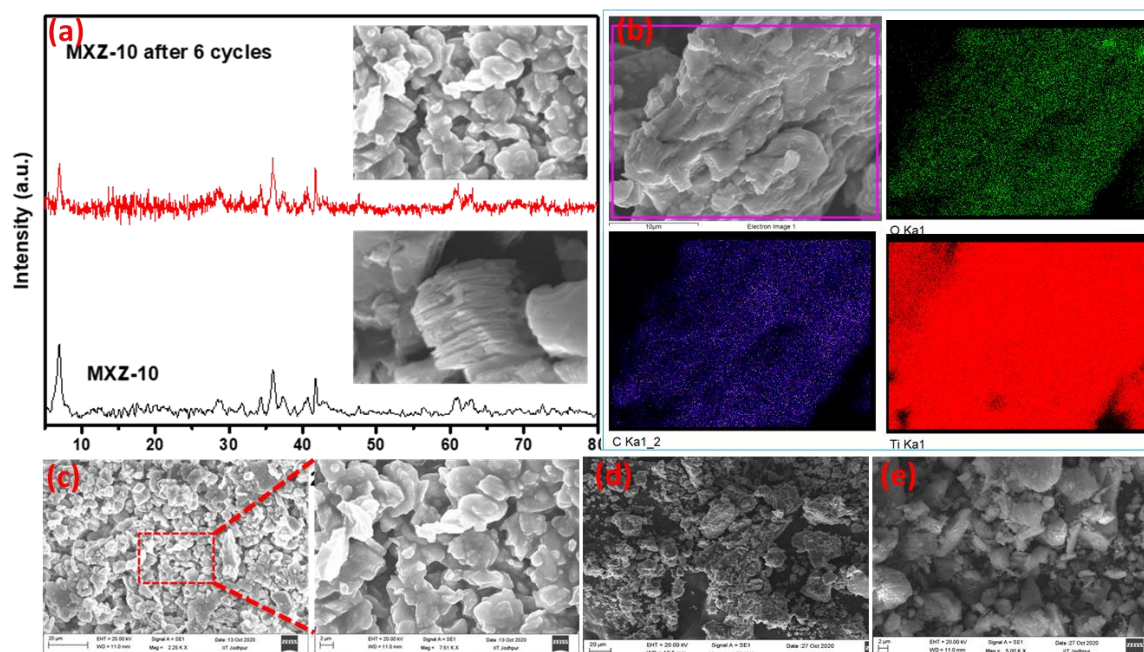


Figure 4.15. XRD of fresh catalyst and reused catalyst of MXZ-10 with SEM images.

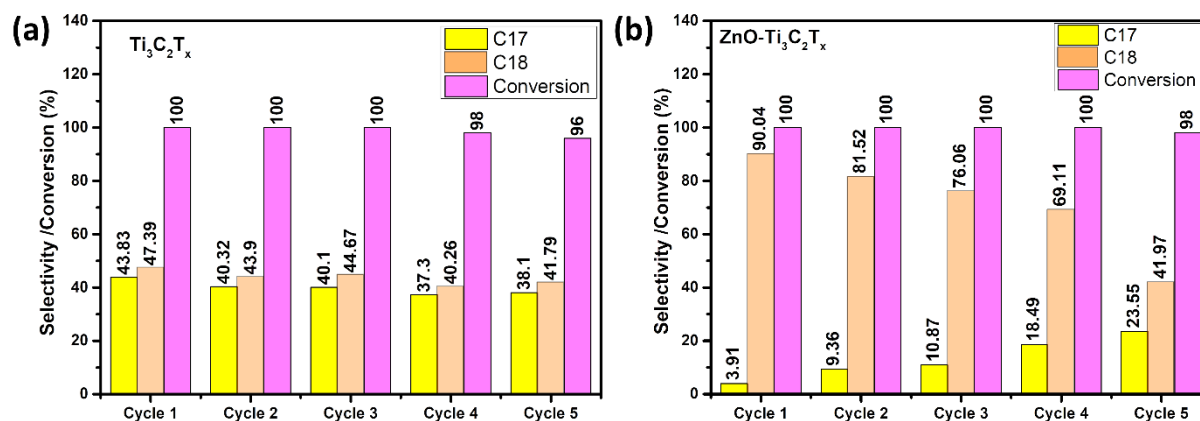


Figure 4.16. Conversion and selectivity of $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{ZnO-Ti}_3\text{C}_2\text{T}_x$ up to 5 cycles (a and b).

4.2.6 Reaction pathway

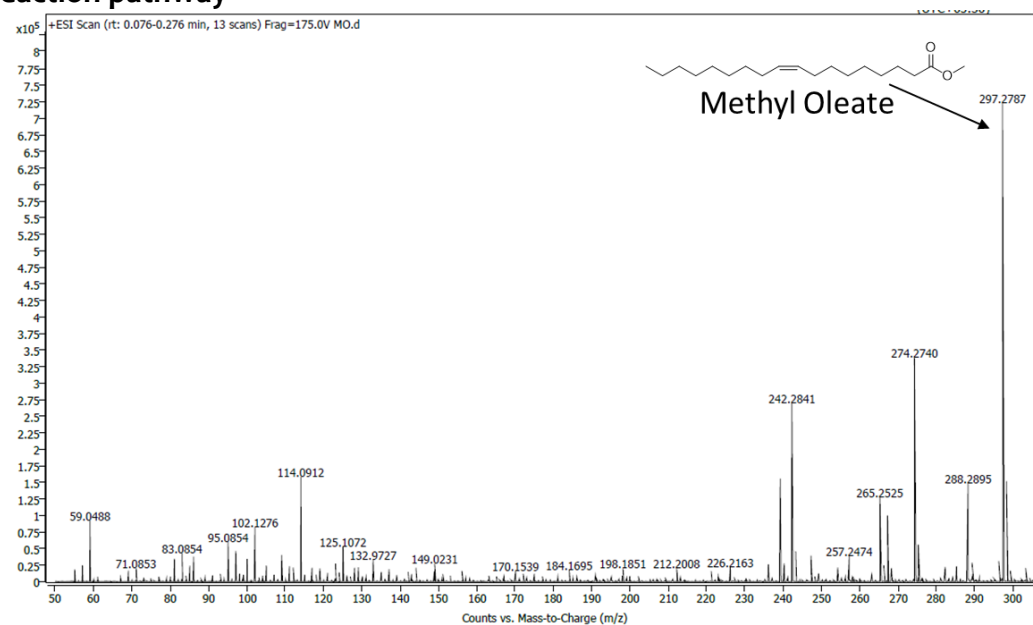


Figure 4.17: HRMS spectrum of pristine methyl oleate. (m/z of 297.2787).

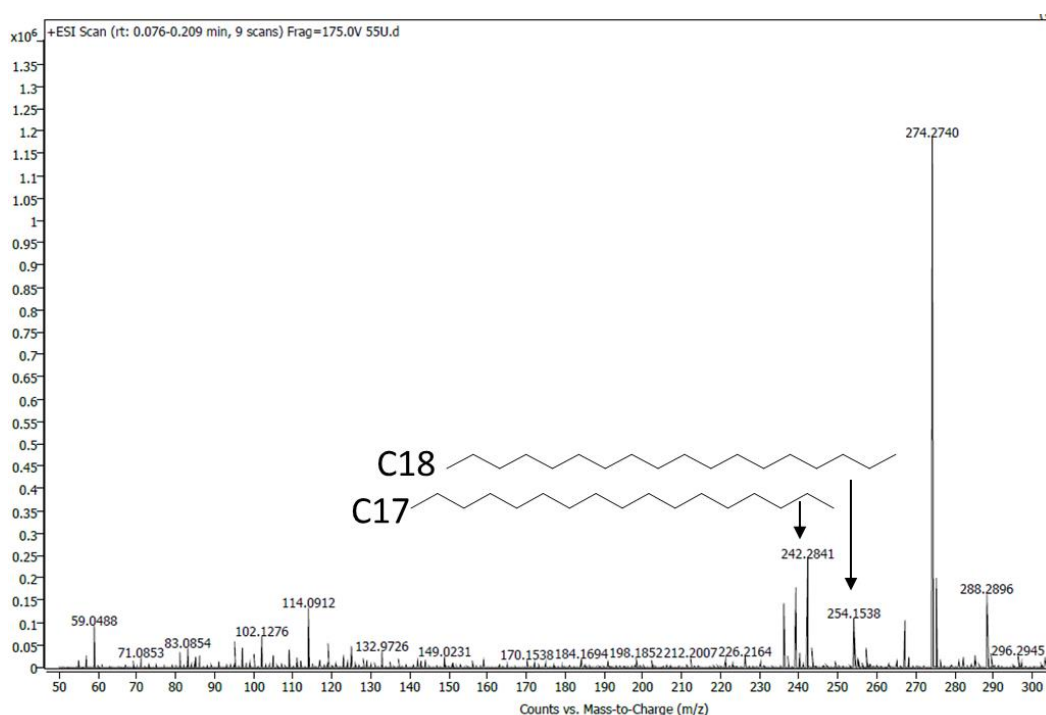


Figure 4.18: HRMS spectrum of reaction after hydrotreatment process using MXZ-10 catalyst (m/z of C18 (254.1538 and C17 (242.2841).

To investigate the MO hydrotreatment pathway, reactions were carried out at 280°C and 30 bar pressure at different time intervals (4, 8 and 13h) to identify the possible intermediates as shown in **Figure 4.17-4.19**. In addition to the C17, C18 and lower hydrocarbon, a trace amount of aldehyde is also detected. Based on the NMR, GC and HRMS data, the proposed possible reaction pathway of the hydrotreatment of the MO and its hydrogenated intermediate products over $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{ZnO-Ti}_3\text{C}_2\text{T}_x$ nanocomposites is outlined in **Scheme 4.20**. (Wang et al., 2019, Krishnapriya et al., 2020) Initially, a saturated n-octadecenoate is formed by hydrogenation during the hydrotreatment of the MO.

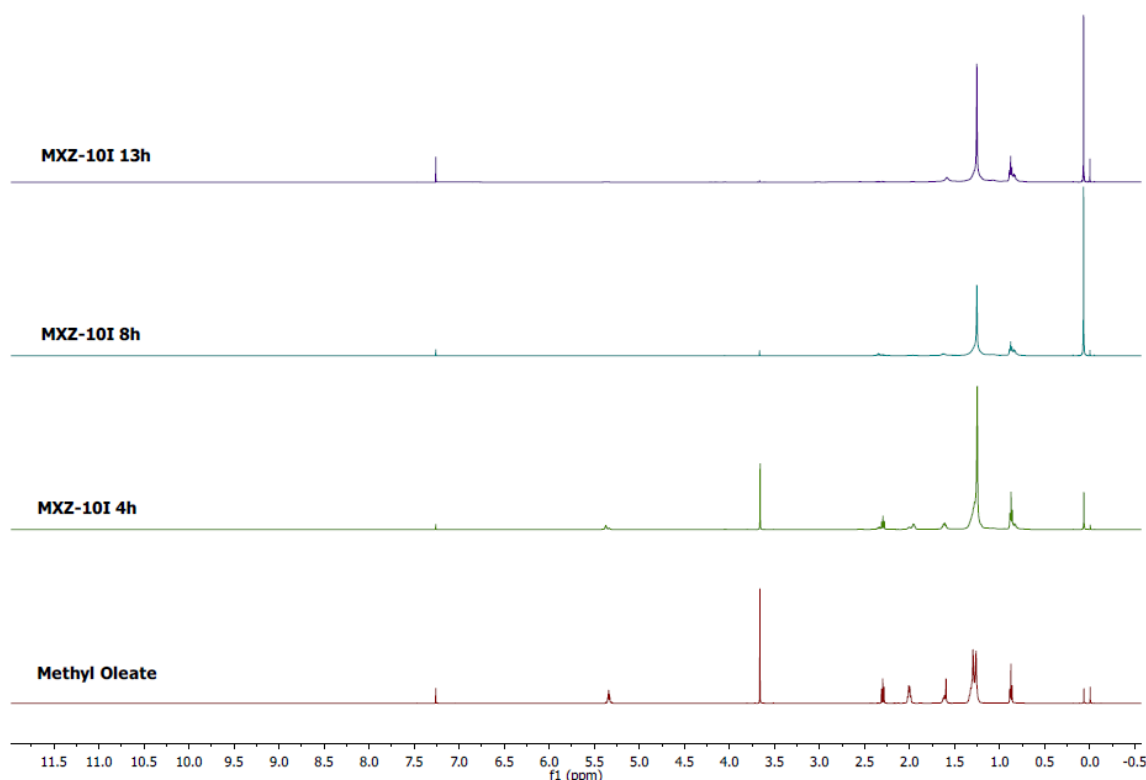


Figure 4.19: ^1H NMR of hydrotreatment reaction with time-dependent study.

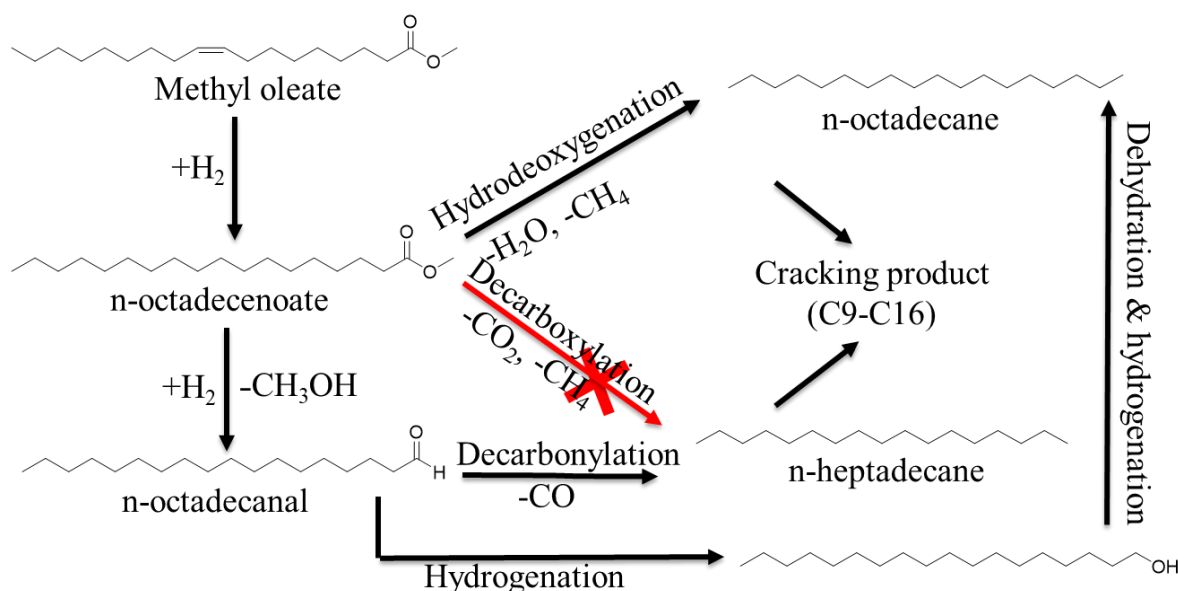


Figure 4.20. Possible reaction pathway of methyl oleate hydrotreatment reaction.

The n-octadecenoate was then hydrogenated into aldehydes as a main pathway rather than hydrolysed into acids because fatty acids methyl ester is not easily convertible into acids via β -elimination (Snåre et al., 2007). These intermediates further proceed through three possible pathways of DCX, DCN, and HDO reactions to yield C17, C18 and lower alkanes. In the decarbonylation and decarboxylation process, n-octadecanal and n-octadecenoate intermediate converted into nC-17 hydrocarbons. As observed in NMR, the reaction proceeding through aldehyde pathway, hence the chances for the decarboxylation process are insignificant. Another possibility is the hydrogenation of n-octadecanal to an alcohol intermediate and subsequently undergoing hydrodeoxygenation to yield n-C18 hydrocarbons via the direct HDO pathway. (Ameen et al., 2017, Coumans and Hensen, 2017b)

4.3 Conclusion

In conclusion, we report Ti₃C₂T_x and ZnO-Ti₃C₂T_x catalytic systems for selective hydrodeoxygenation of methyl oleate as a model compound for bio-oil up-gradation to diesel-grade hydrocarbons. The developed catalyst materials were characterized by XRD, XPS, TEM, and EDX; which revealed the successful formation of the preferred catalyst. The catalyst activities and efficiencies were tested and optimized systematically by considering the effect of catalytic loading, solvent, reaction time, temperature, and pressure. It is found that higher catalytic loading initiates the cracking process while lower catalyst loading gives intermediates aldehyde (-CHO), and alcohol (-OH) with less selectivity towards the desired n-C17 and n-C18 products. We understood that when the ZnO-Ti₃C₂T_x catalyst (at 280°, 30 bar and 13h) was applied for selective HDO reaction, the synergy of metal oxide with 2D MXene resulted in 90.04% selectivity with 100% conversion. Surprisingly, the catalysts showed excellent recyclability without significant drop-in catalytic activity up to 5 test cycles. High HDO selectivity is very promising by reducing carbon dioxide footprint and carbon economy principle in terms of future biofuel production via the green chemistry route. Advantageously, the solvent-free condition offers an excellent and green method for diesel-grade hydrocarbon production from biomass.

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