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Novel tetra propyl/butyl ammonium encapsulated Keggin-type polyoxotungstates: synthesis, structural characterization, and catalytic capability in oxidative cleavage of unsaturated fatty acids

Amir Enferadi-Kerenkan, Arnaud Gandon, and Trong-On Do *

Department of Chemical Engineering, Université Laval, Québec, G1V 0A6, Canada.

* E-mail: trong-on.do@gch.ulaval.ca

Supporting Information

S1. Derivatization process prior to GC-MS analysis

Gas chromatography-mass spectrometry (GC-MS) analysis was used for the separation, identification, and quantification of the products after the reaction. Fundamentally, fatty acids in their free form are difficult and fallible to analyze with GC, because these highly polar compounds tend to form hydrogen bonds with the stationary phase in GC columns, leading to adsorption issues. Reducing their polarity make them more amenable for analysis. Converting fatty acids to fatty acid methyl esters is the most common method for preparation of fatty acids prior to GC analysis, because methyl esters offer excellent stability, and provide quick and quantitative samples for analysis.

After a typical oxidative cleavage reaction, the products mixture underwent a derivatization reaction, in which the expectedly produced azelaic and pelargonic acids, and possibly unreacted oleic acid were esterified to dimethyl azelate, methyl pelargonate, and methyl oleate, respectively. The esterification, briefly, involved heating the fatty acids in presence of an acid catalyst, boron trifluoride, in methanol to give fatty acid methyl esters. First, BF_3 protonates an oxygen atom of the carboxyl group making the acid much more reactive to nucleophiles, and then, methanol molecule combines with the protonated acid, to give the ester products (Scheme S1).

Typically, BF_3-methanol (5 mL) (10% w/w, Sigma-Aldrich Co.) was, firstly, added to the fatty acids mixture, in which the total weight of fatty acids is less than 400 mg. Then, the mixture was heated to 80 °C for 15 min, followed by cooling down at room temperature for about 20 min. The ester products were extracted by adding 2 mL petroleum ether (Fisher Scientific Co.) and 2 mL water. After carefully removing the organic (upper) layer, the aqueous phase underwent the second extraction. Finally, the obtained organic phase was dehydrated by sodium sulfate (anhydrous, ≥99%, Sigma-Aldrich Co.) and then the solvent was removed by passing a steady stream of dry air. After properly dilution, the obtained esterified mixture was ready for injection to GC-MS.

S2. Quantitative analysis of the reaction products

A typical derivatized sample, expectedly including dimethyl azelate, methyl pelargonate, and possibly methyl oleate, was injected to the GC-MS which had been previously calibrated by analytical standards of these methyl esters (all were purchased from Sigma-Aldrich Co.). A constant and exact amount of 1.0 µL was injected each time, and the injection was repeated at least four times for each sample to be averaged.

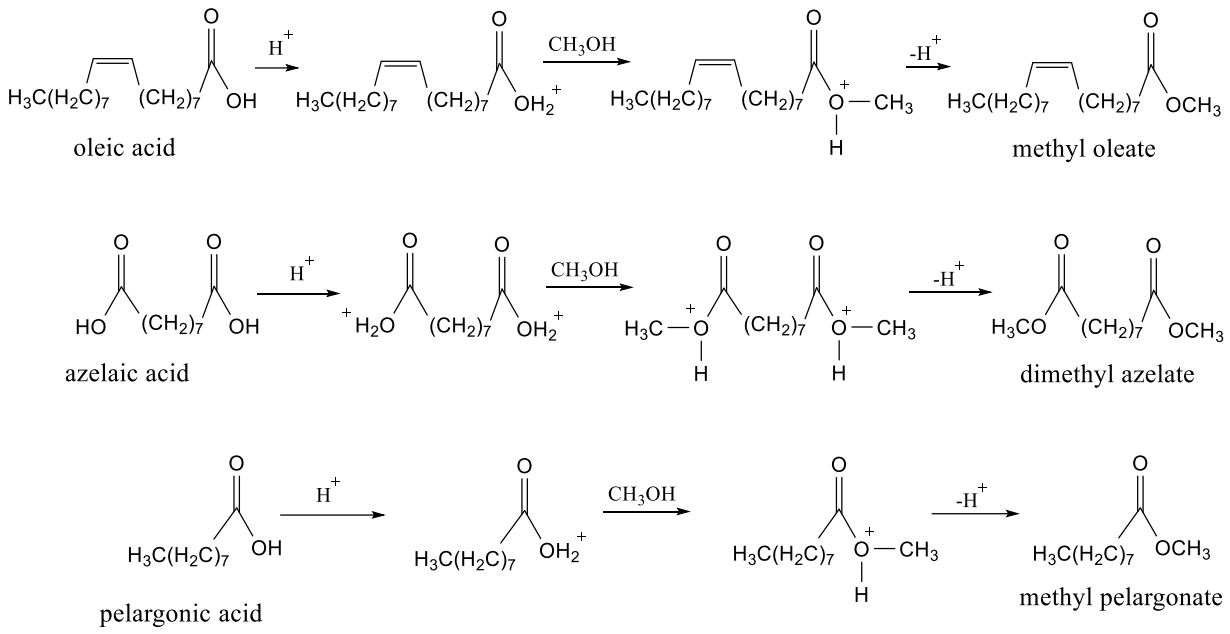
The obtained chromatograms of products for the catalytic tests in Table 1 are shown in Figures S7−S10. Owing to the carefully chosen column type and operating conditions of GC (see section S3), the obtained peaks had excellent shape and sharpness, which lead to reliable results. Based on peak areas in these chromatograms and the calibration curves of the standard methyl esters (which showed excellent linearity), conversion and yields of the oxidative cleavage reaction in Table 1 were calculated. Yield, in this work, is defined as the amount of a product formed per total amount of oleic acid consumed (both in moles). Reproducibility of the results in this Table have been verified by performing at least 3 runs over each catalyst.

The properly adjusted temperature programming allowed separation of methyl pelargonate, dimethyl azelate, and methyl oleate with discrete retention times (R_t) of 10.4, 15.8, and 26.8 min, respectively. Some other peaks were also observed in the chromatograms, indicating presence of by-products, which were qualitatively analyzed by MS, as follows. Small and often negligible peaks in e.g. R_t= 6.8, 8.9, 11.2, and 16.7 min belonged to octanal, methyl esters of hexanoic and octanoic acids, and 9,10-dihydroxy octadecanoic acid, respectively, which were produced by impurities of the reactants and/or insignificant side reactions (e.g. hydroxylation). Two relatively more considerable peaks in R_t= 8.6 and 13.8 min belonged to nonanal and 9-oxononanoic acid, respectively, which were produced by partial-oxidation of oleic acid. Since after minute 30 no significant peak was obtained, the chromatograms in Figures S1-S8 have been monitored up to R_t= 30 min.

It should be noted that such by-products like 9-oxononanoic acid, which are the direct result of involvement of carboxylic group in the reaction, has made oxidative cleavage of unsaturated fatty acids, compared to alkenes and cyclic olefins, more complicated and investigation of their reaction mechanism more difficult.[11-13] It makes more sense given the fact that 9-oxononanoic acid is not commercially available (in known chemical provider companies), which makes calibration of chromatography systems by the analytical standard of this chemical, and consequently its quantitative analysis by these systems impossible. We are currently working on kinetic studies to learn about the competition between partial and over-oxidation of oleic acid and consequently, propose an accurate mechanism showing how both oleic acid and hydrogen peroxide can be activated by the prepared catalysts.

S3. GC-MS specifications

The GC-MS included a Hewlett-Packard HP 5890 series GC system and MSD Hewlett-Packard model 5970. GC system was equipped with Zebron ZB-5MS capillary column (30 m × 0.25 mm × 0.25 mm). Helium was used as a carrier gas with the flow rate of 30 mL/min. A split ratio of 20:1 was fixed. The front inlet temperature was 280 °C. The oven temperature program consisted of maintaining at 50 °C for 2 min, then a ramp rate of 10 °C/min to 160 °C following by a hold-up time of 1 min, and further increase with the rate of 5°C/min to 290 °C. Direct injection by a 5.0 µL syringe (SGE fixed needle, 23-26 gauge/42mm L/Cone Tip, Phenomenex Co.) was employed with 1.0 µL injection amount for each run. HP Chemstation software was used to analyze data.



Scheme S1. Esterification of oleic, azelaic, and pelargonic acids with methanol to methyl oleate, dimethyl azelate, and methyl pelargonate, respectively, over an acid catalyst, BF_3.

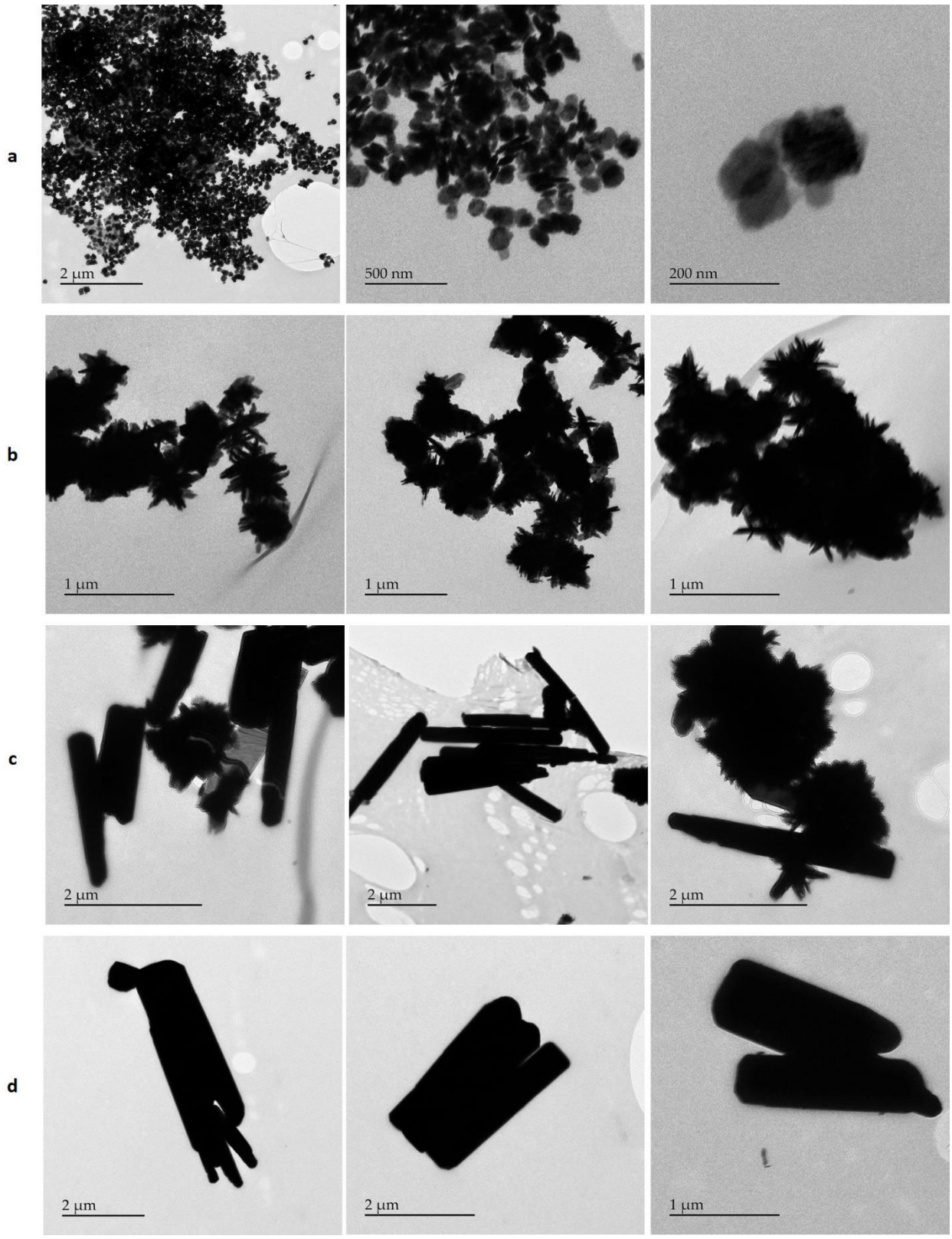


Figure S1. Additional TEM images of (a) TO, (b) TO-TMA1/2, (c) TO-TMA, and (d) TO-TMA2.

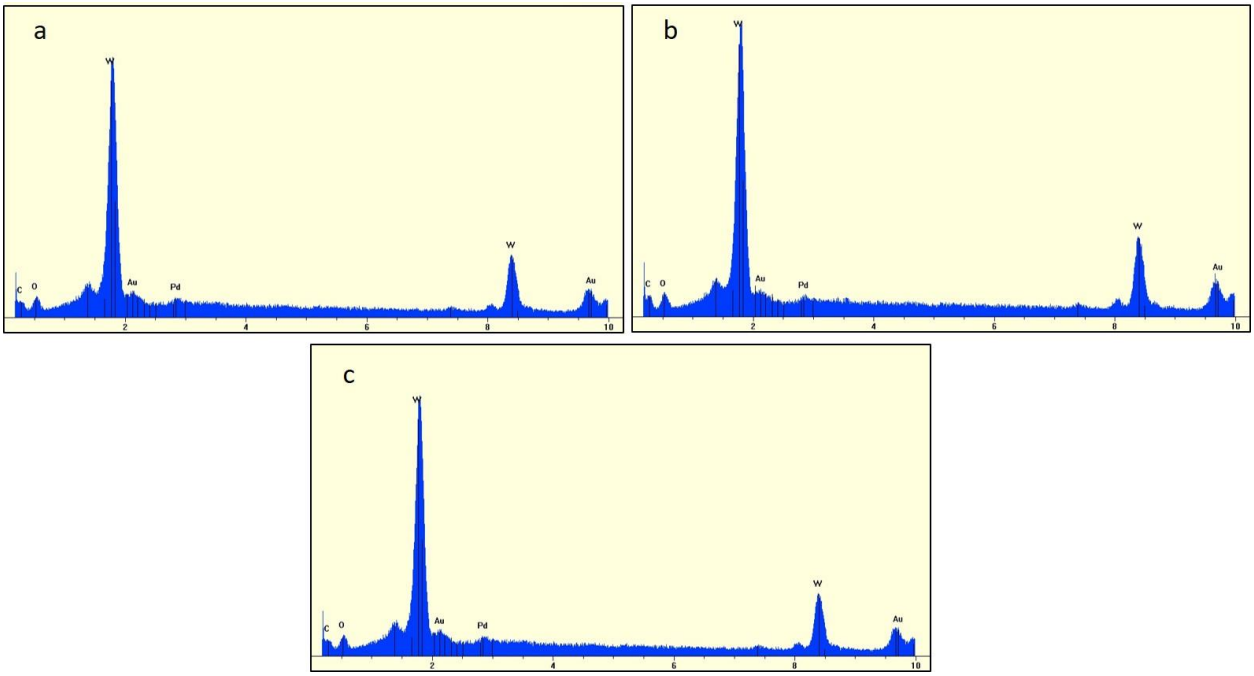


Figure S2. EDS spectra of (a) TO-TMA, (b) TO-TPA, and (c) TO-TBA (Au and Pd are from the instrument).

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-6.56	Peak 1:	-6.56	100.0	4.29
Zeta Deviation (mV):	4.29	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm):	0.328	Peak 3:	0.00	0.0	0.00

Result quality : Good

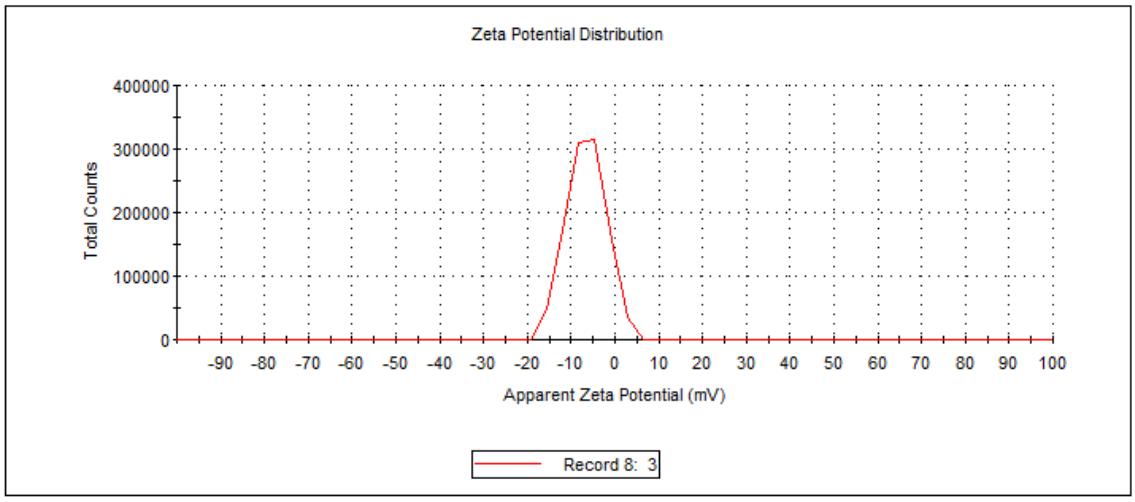


Figure S3. Surface zeta potential of TO particles (pH 1.7−1.9).

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-35.9	Peak 1:	-35.9	100.0	7.25
Zeta Deviation (mV):	7.25	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm):	0.0526	Peak 3:	0.00	0.0	0.00

Result quality : Good

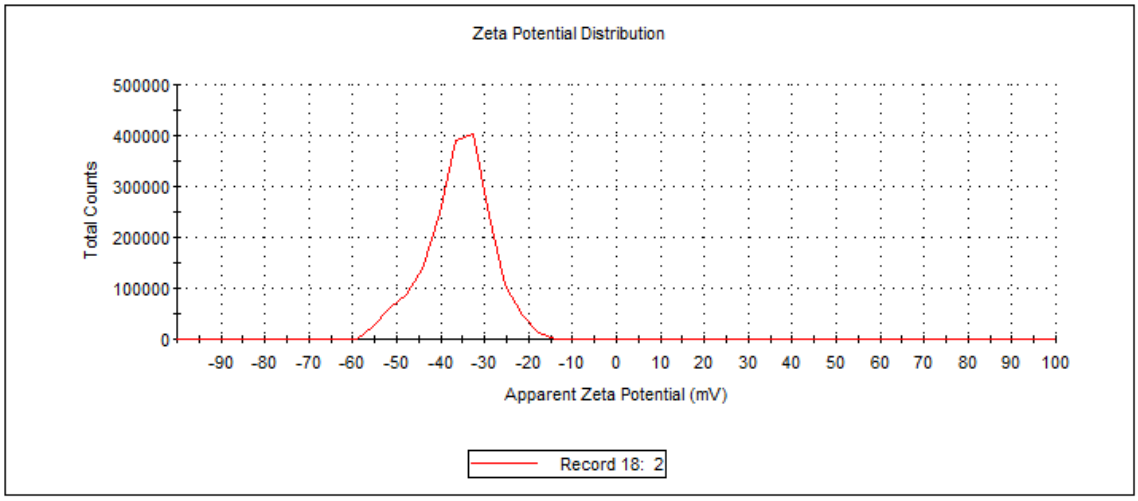


Figure S4. Surface zeta potential of TO-TMA particles (pH 1.7−1.9).

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-41.3	Peak 1:	-41.3	100.0	8.18
Zeta Deviation (mV):	8.18	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm):	0.0437	Peak 3:	0.00	0.0	0.00

Result quality : Good

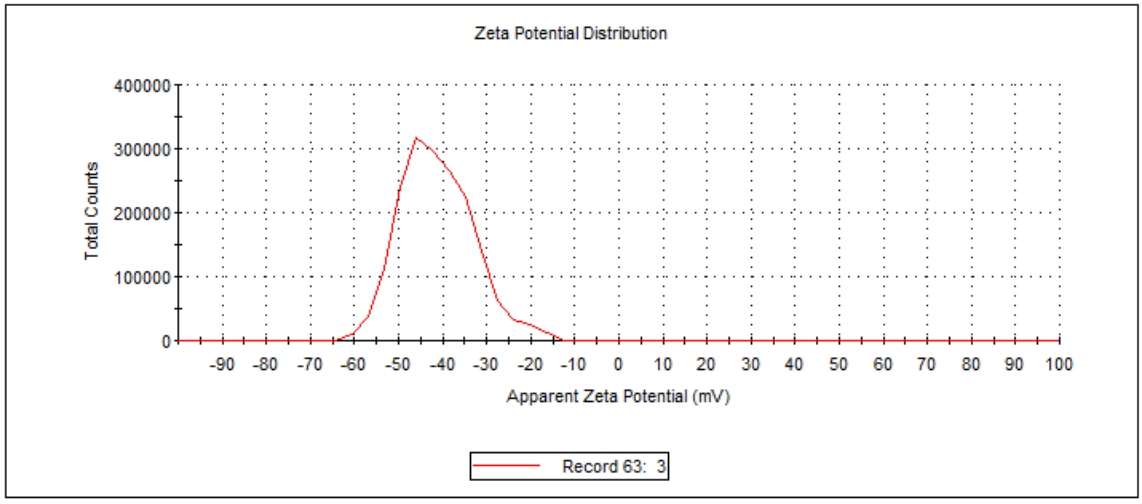


Figure S5. Surface zeta potential of TO-TPA particles (pH 1.7−1.9).

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-49.4	Peak 1:	-49.4	100.0	8.13
Zeta Deviation (mV):	8.13	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm):	0.0414	Peak 3:	0.00	0.0	0.00

Result quality : Good

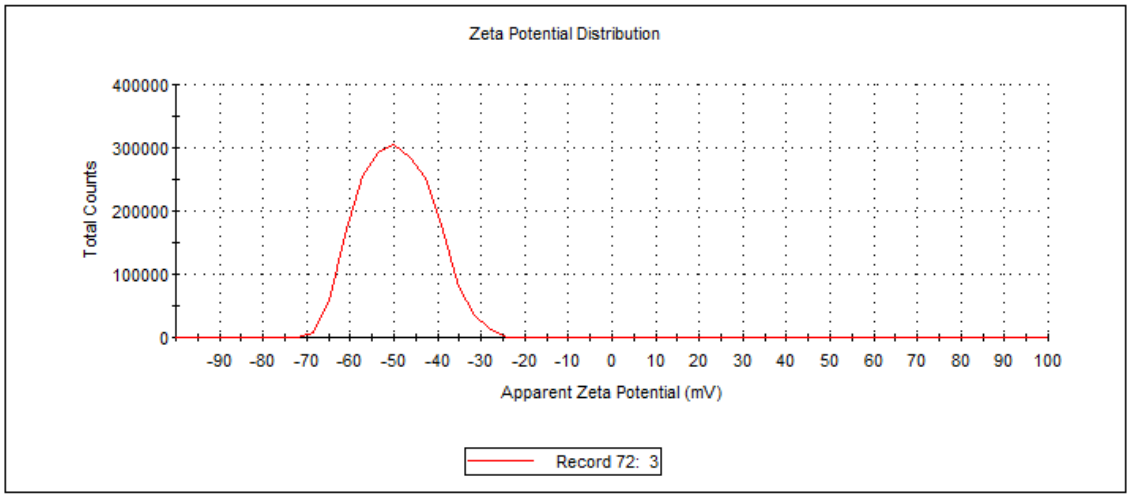


Figure S6. Surface zeta potential of TO-TBA particles (pH 1.7−1.9).

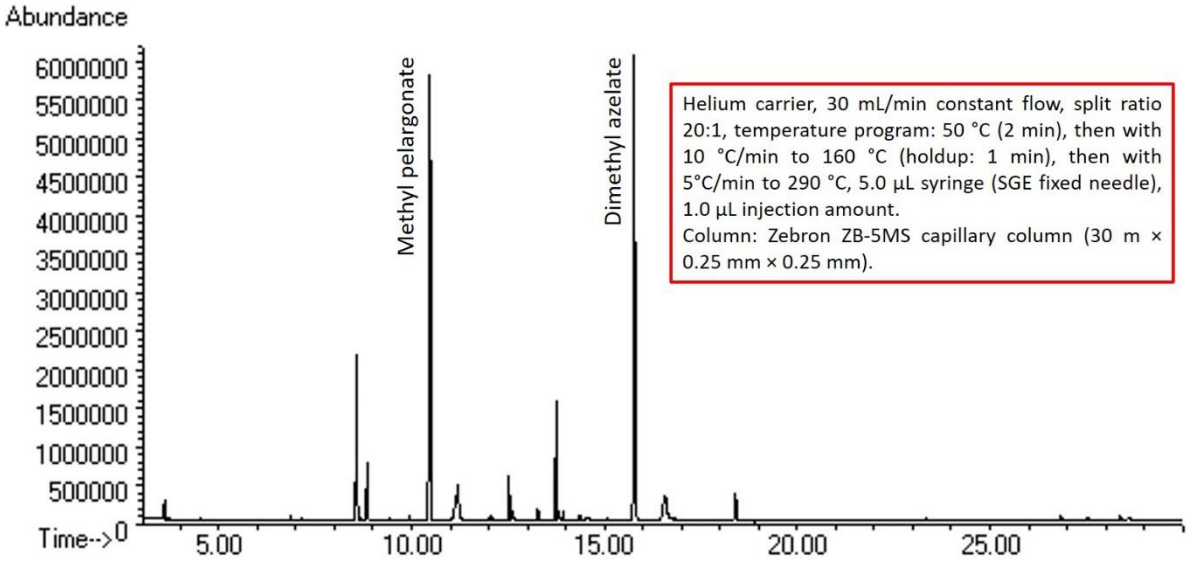


Figure S7. Gas chromatogram of products of the catalytic test over TO catalyst.

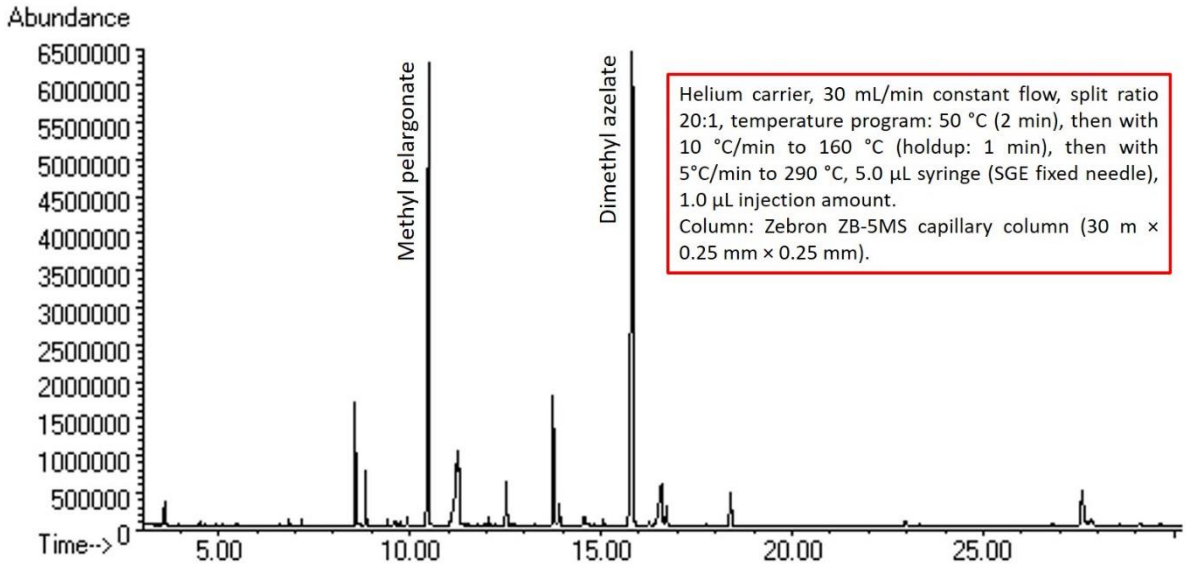


Figure S8. Gas chromatogram of products of the catalytic test over TO-TMA catalyst.

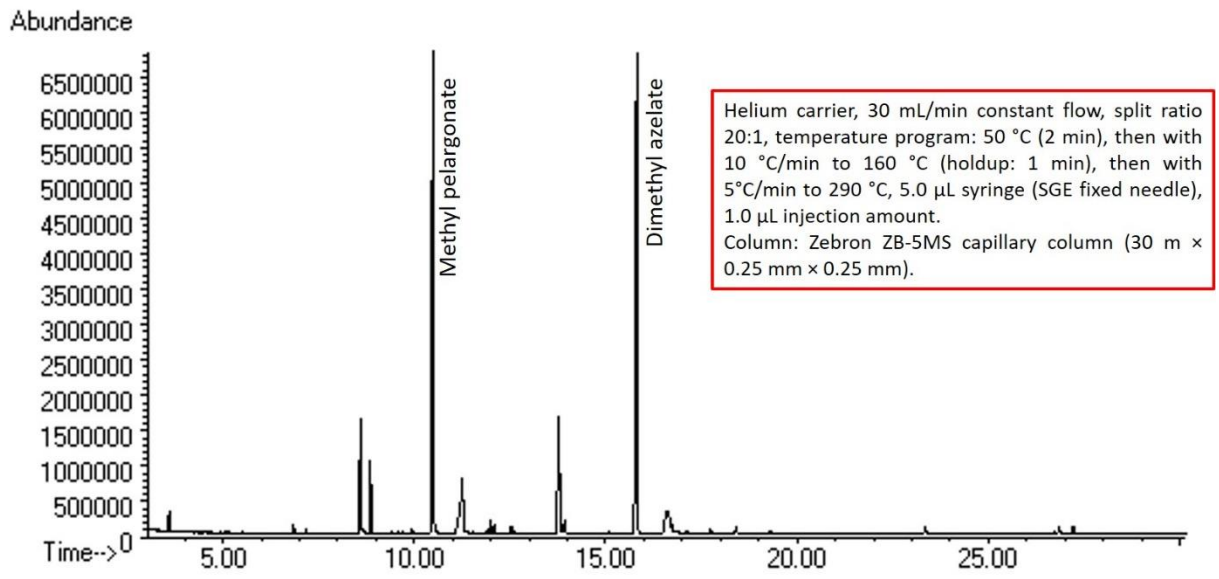


Figure S9. Gas chromatogram of products of the catalytic test over TO-TPA catalyst.

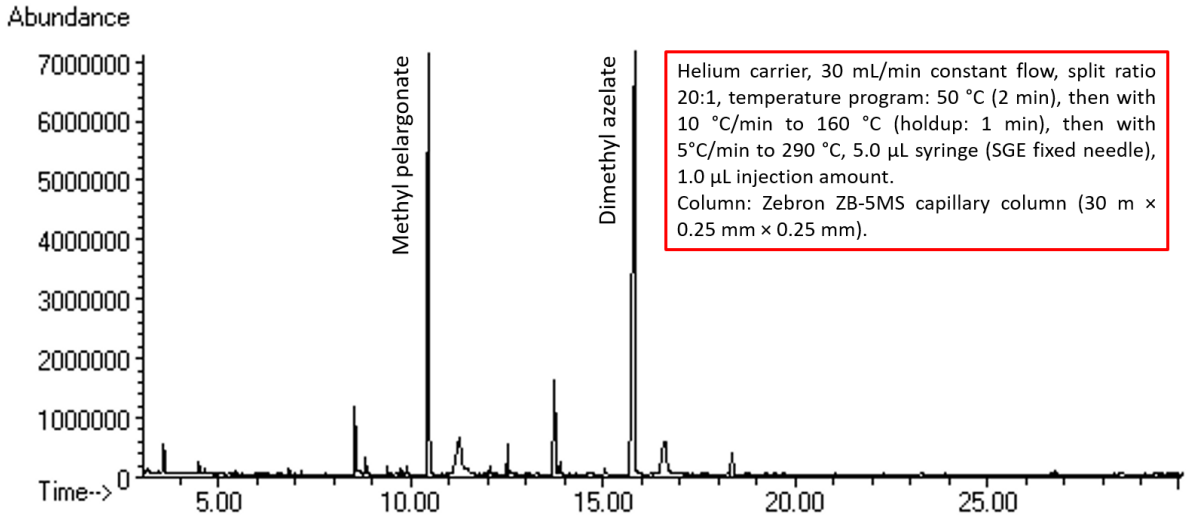


Figure S10. Gas chromatogram of products of the catalytic test over TO-TBA catalyst.

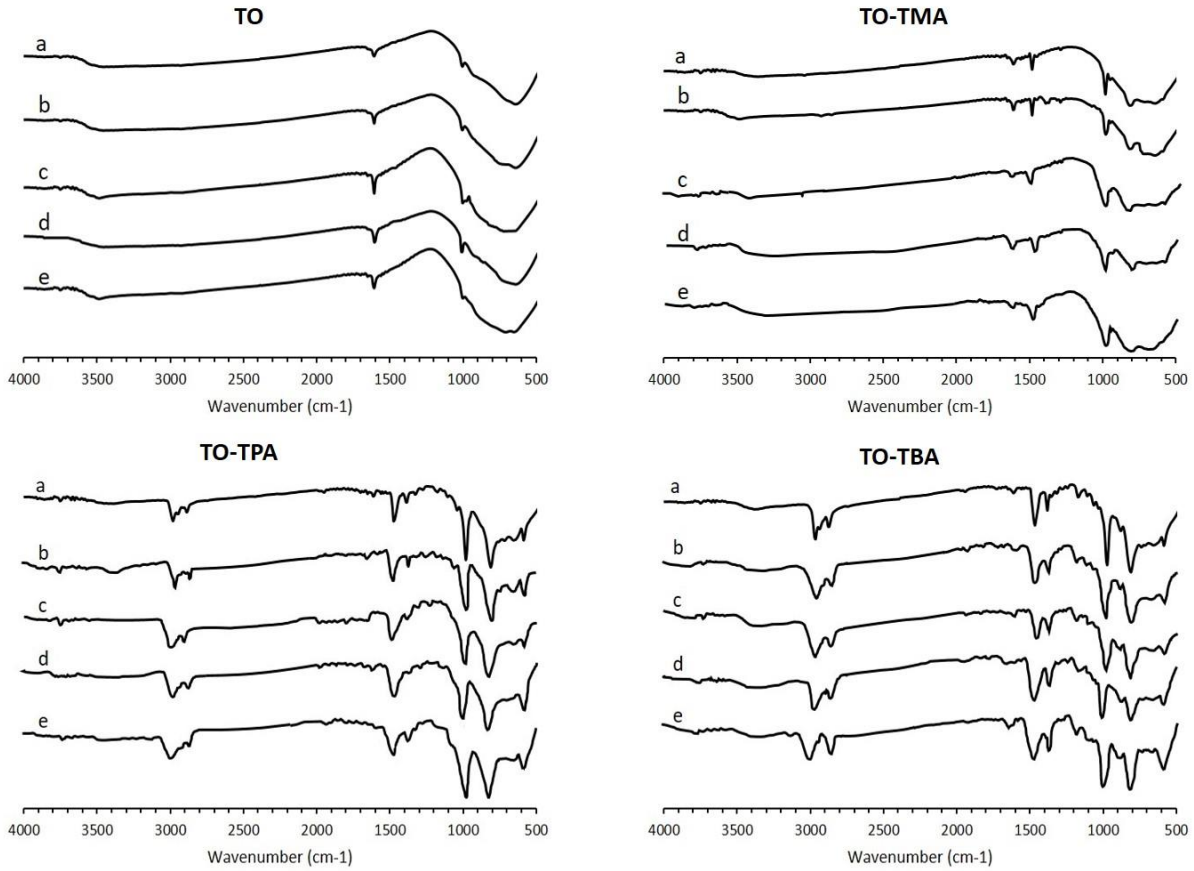


Figure S11. FTIR spectra of the catalysts: (a) before reaction, (b) after 1st cycle, (c) after 2nd cycle, (d) after 3rd cycle, and (e) after 4th cycle.

Table S1. Assignments of the FTIR absorption bands of the prepared samples

Absorption bands (cm^{-1})	Assignment	Remarks	Ref.
587	W (O_2)	Observed in TO-TPA and TO-TBA	20, 25
633−649	ν (W-O)	Observed in all the samples	20-23
811	ν (W-O)	Observed in TO-TMA, TO-TPA, and TO-TBA	20, 26, 27
880	ν (W-O)	Observed in TO-TBA	20, 26, 27
973−1019	ν (W=O)	Observed sharply in TO-TMA, TO-TPA, and TO-TBA, and weakly in TO	21, 23-25
1382	CH_2	Observed in TO-TPA and TO-TBA	[a-d]
1475−1482	ν (CH_3)	Observed in TO-TMA, TO-TPA, and TO-TBA	[a-d]
1606−1614	δ (H-O-H)	Observed in all the samples	21-23, 25
2873−2981	ν (CH_2)	Observed in TO-TPA and TO-TBA	[a-d]
3390-3483	ν (H-O-H)	Observed in all the samples	21-23, 25

Additional references:

[a] Huang, et al., *Journal of Materials Chemistry*, 2001, 11, 610.

[b] C.F.WilcoxJr, et al., *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 1996, 52, 207.

[c] R. Lu, et al., *Journal of Physical Chemistry B*, 2005, 109, 14118.

[d] C. Coury, et al., *Atmospheric Environment*, 2008, 42, 5923.

Table S2. Elemental analysis (C/H/N/S analysis) results for the prepared hybrid materials [a].

Sample		% Nitrogen	% Carbon	% Hydrogen	% Sulphur
TO-TMA	1st analysis	0.76	2.75	1.14	0.00
	Duplicate	0.83	2.99	1.14	0.00
	Average	0.80	2.87	1.14	0.00
TO-TPA	1st analysis	1.08	11.49	2.62	0.00
	Duplicate	1.06	11.21	2.47	0.00
	Average	1.07	11.35	2.55	0.00
TO-TBA	1st analysis	1.21	17.46	3.43	0.00
	Duplicate	1.20	17.17	3.43	0.00
	Average	1.21	17.31	3.43	0.00

[a] The detection limits for the analyses are the following: 0.3 % for C, H, N and 1.0 % for S. The ratios between Keggin clusters [$H_nW_{12}O_{40}$], incorporated organic cations (TPA^+ or TBA^+), and associated water molecules in compositions of TO-TPA and TO-TBA were calculated based on C% and H%. Accordingly, the stoichiometric formulas of these hybrid compounds were suggested. Then, the accuracy was validated by determining the amount of N% from the obtained formula. This gives 1.10 and 1.26% for TO-TPA and TO-TBA, respectively, which are in good agreement with those obtained from the elemental analysis (above Table, 1.07 and 1.21%, respectively).

Table S3. BET surface areas of the prepared samples.

Sample	TO	TO-TMA	TO-TPA	TO-TBA
S_{BET} (m^2/g)	16.8	13.3	≤ 10	≤ 10

Table S4. Weight losses of the synthesized catalysts during the different cycles of the reaction

Reaction cycle	TO	TO-TMA	TO-TPA	TO-TBA
1st	2.3	2.1	1.9	2
2nd	2.1	1.7	2.1	1.8
3rd	1.9	1.3	1.5	1.2
4th	2.1	1.7	1.6	1.6