Electronic Supplementary Information (ESI)

for

Heterogeneous Chemistry of Methyl Ethyl Ketone on Mineral Oxide Surfaces: Impacts of Relative Humidity and Nitrogen Dioxide on Product Formation

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ESI contains 6 figures (Figures S1-S5) and 3 tables (Table S1-S3).

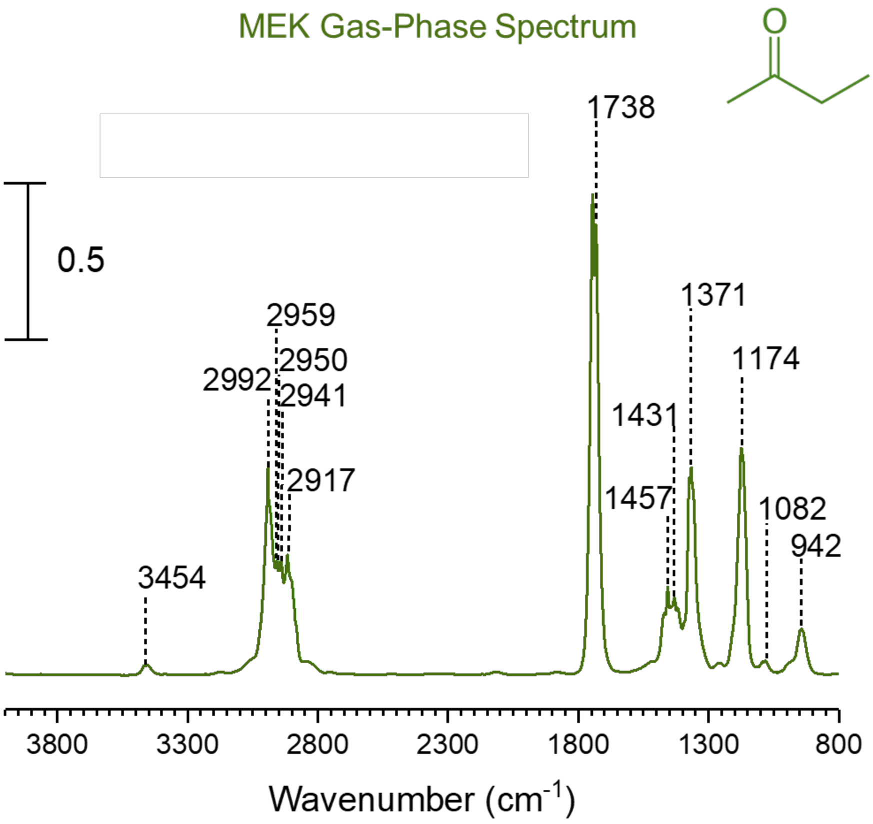

Figure S1: Gas-phase FTIR spectrum of Methyl Ethyl Ketone (MEK), 200 mTorr in the spectral region from 800 - 4000 cm^{-1}. The peak at 3454 cm^{-1} is assigned to C=O bond overtone, whereas the peak at 1738 cm^{-1} is assigned to C=O bond stretching vibration. The peaks at 2992, 2959, 2950, 2941, and 2917 cm^{-1} are assigned to various C-H stretching bond vibrations, and the peak at 1457, 1431 and 1371 cm^{-1} are assigned to C-H bond bending vibrations. 1174 cm^{-1} is assigned to C-C bond vibration. Peak assignments were based on existing literature assignments[1] and Computational Chemistry Calculations (phase: gas-phase, method: ωB97X-D, basis set: 6-31G*, package used: SPARTAN'20 Mechanics Program 20.1.4). Absorption scale is provided in the top left corner.

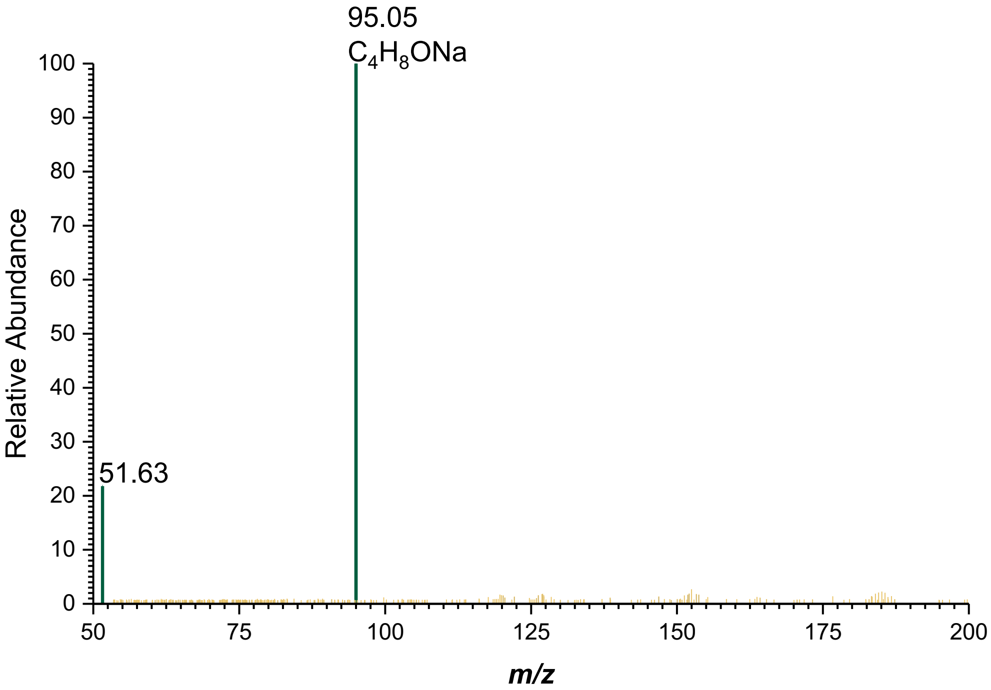

Figure S2: HRMS patterns of 70 ppm MEK standard in methanol. MEK remains as the sodated monomer during analysis. At very high MEK standard concentrations (1000 ppm), MEK forms a sodated dimer (*m/z* 167.10). However, on mineral surfaces, even with lower pressures used, significantly larger intensities of a MEK dimer were observed indicating surface-driven dimerization. Importantly, MS/MS fragmentation of *m/z* = 167.10 from MEK standard (1000 ppm) produced only one fragment at *m/z* = 95.05 for MEK monomer, whereas for *m/z* = 167.10 peak observed on mineral surfaces produced other fragments as shown in **Table S1**. This indicates that at higher concentrations, the standard MEK sample produced a clustered 'dimer' under MS conditions,[2] while on mineral surfaces, MEK produced a true dimer with the structure of compound **1**. Additionally, other oligomers observed on mineral surfaces were neither detected in 70 ppm nor 1000 ppm MEK standards in methanol. Moreover, no additional products were identified in MEK standard samples confirming that it doesn't react with methanol at either solvent extraction or HRMS analysis steps.

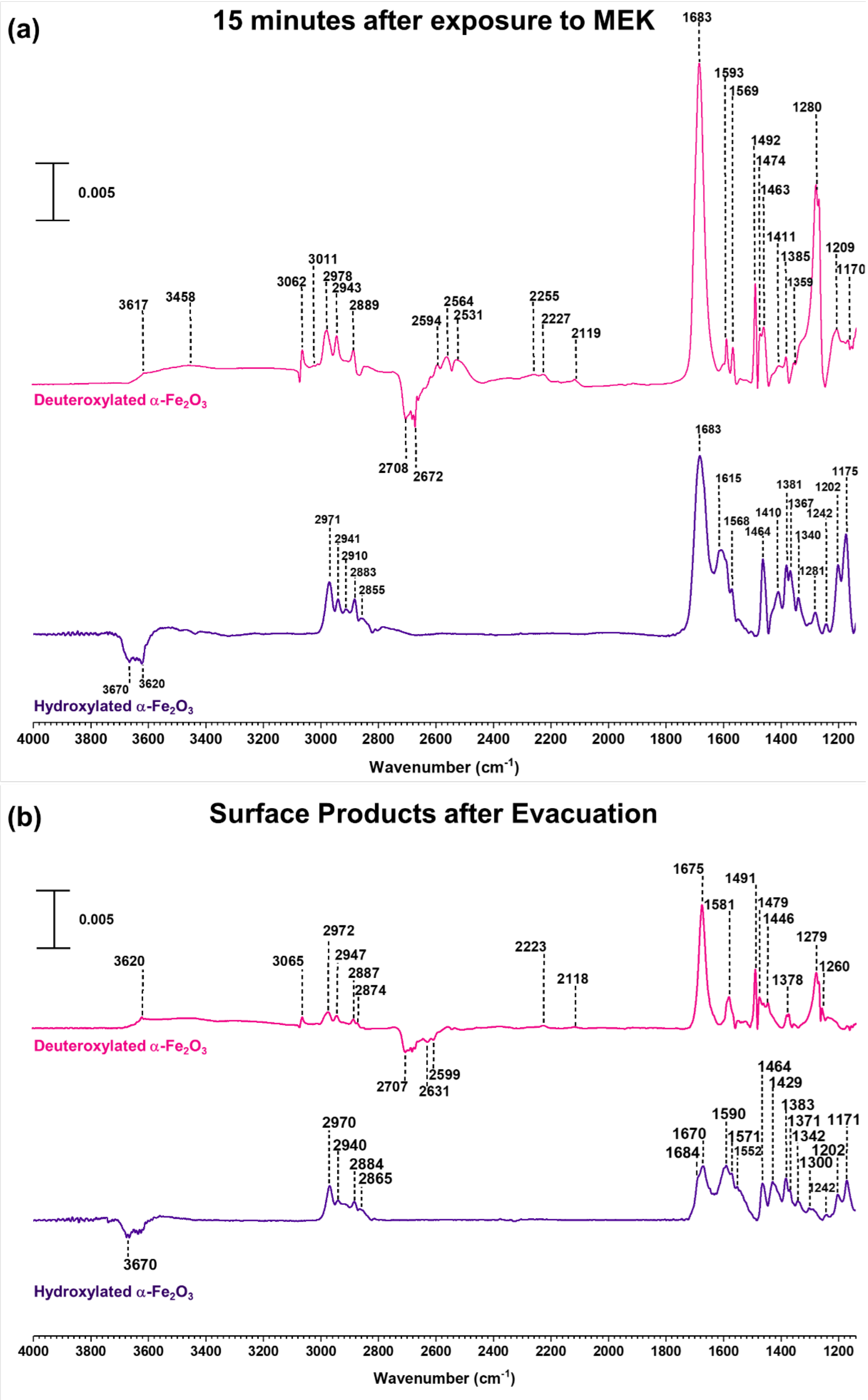

Figure S3: FTIR spectra of adsorbed Methyl Ethyl Ketone (MEK), 100 mTorr (a) after 15 minutes of exposure on hydroxylated and deuteroxylated α-Fe_2O_3 surfaces and (b) after evacuating overnight, in the spectral region from 1140 - 4000 cm^{-1}. The absorbance scale is shown in the top left corner.

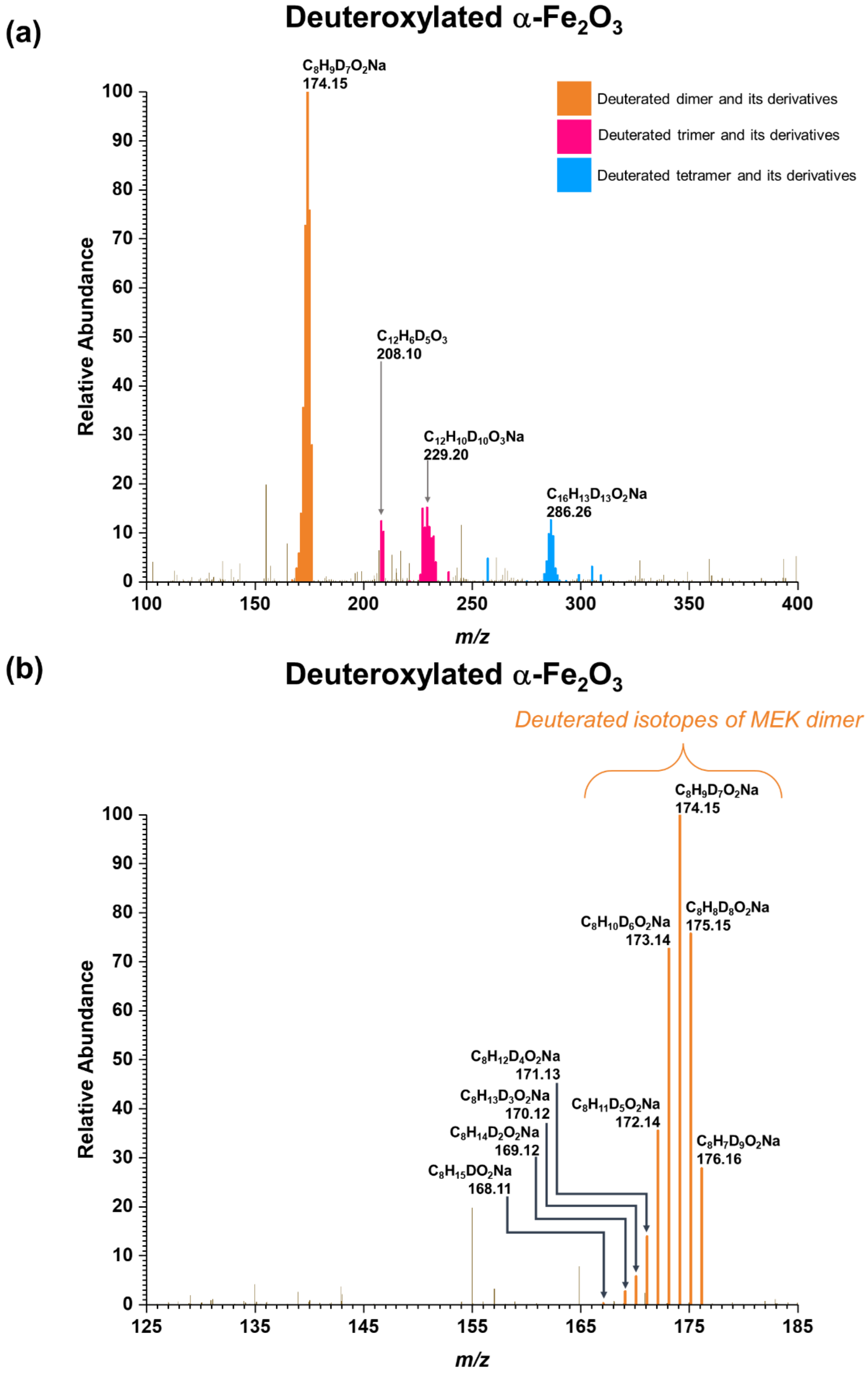

Figure S4: HRMS patterns of surface products formed upon adsorption on MEK on deuteroxylated α-Fe_2O_3. (a) Deuterated isotopes of and their dehydration products corresponding to MEK dimer, trimer, and tetramer. (b) Isotope variation of MEK dimer.

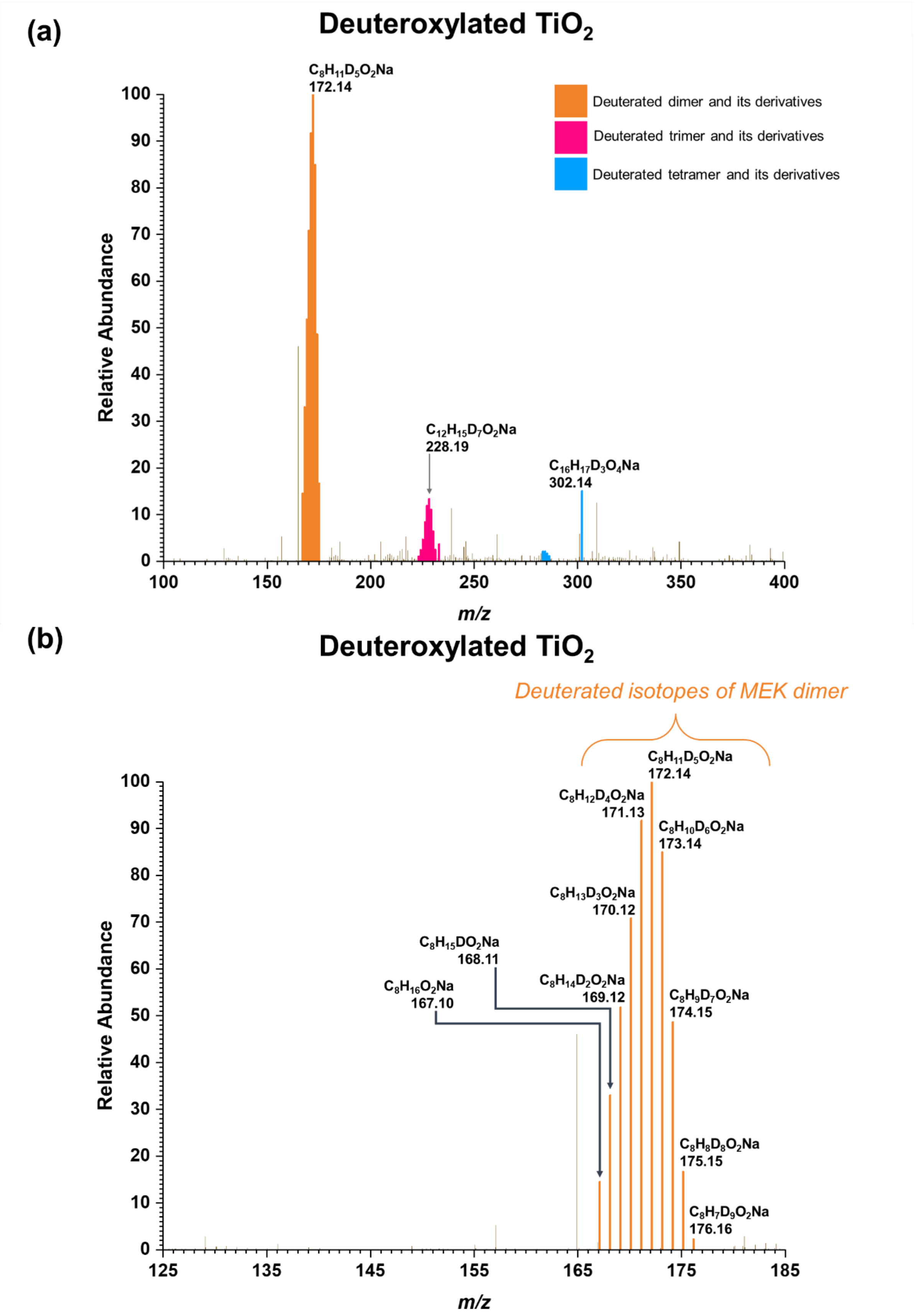

Figure S5: HRMS patterns of surface products formed upon adsorption on MEK on deuteroxylated TiO_2. (a) Deuterated isotopes of and their dehydration products corresponding to MEK dimer, trimer, and tetramer. (b) Isotope variation of MEK dimer.

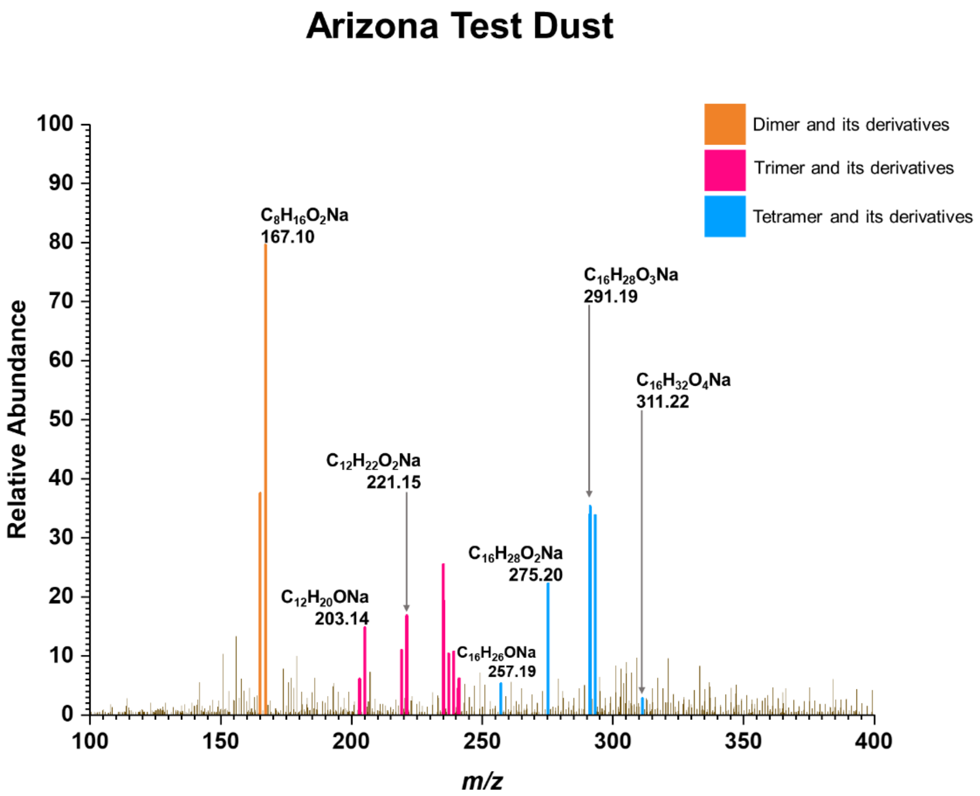

Figure S6: HRMS patterns of surface products formed upon adsorption on MEK on Arizona Test Dust (AZTD).

Table S1: MS/MS Analysis of Identified Compounds.

ID	Parent Peak, Observed Formula	Fragments	Formula of the Fragment
1000 ppm MEK standard	167.10, $C_8H_{16}O_2Na$	95.05	C_4H_8ONa
1	167.10, $C_8H_{16}O_2Na$	95.05	C_4H_8ONa
		127.11	$C_8H_{15}O$
		138.03	$C_6H_{11}O_2Na$
2	239.16, $C_{12}H_{24}O_3Na$	221.15	$C_{12}H_{22}O_2Na$
		237.15	$C_{12}H_{22}O_3Na$
	221.15, $C_{12}H_{22}O_2Na$	95.05	C_4H_8ONa
		151.07	$C_7H_{12}O_2Na$
		203.14	$C_{12}H_{20}ONa$
		219.14	$C_{12}H_{20}O_2Na$
5	311.22, $C_{16}H_{32}O_4Na$	163.07	$C_8H_{12}O_2$
6	293.20, $C_{16}H_{30}O_3$	291.19	$C_{16}H_{28}O_3$
		275.20	$C_{16}H_{28}O_2Na$
	275.20, $C_{16}H_{28}O_2Na$	273.19	$C_{16}H_{26}O_2Na$
		257.19	$C_{16}H_{26}ONa$
9	139.07, $C_6H_{12}O_2Na$	137.06	$C_6H_{10}O_2Na$
		135.04	$C_6H_8O_2Na$
11	153.09, $C_7H_{14}O_2Na$	151.07	$C_7H_{12}O_2Na$
12	283.19, $C_{14}H_{28}O_4Na$	281.17	$C_{14}H_{26}O_4Na$
13	265.18, $C_{14}H_{26}O_3Na$	263.16	$C_{14}H_{24}O_3Na$
14	247.17, $C_{14}H_{24}O_2Na$	218.12	$C_{12}H_{19}O_2Na$
		245.15	$C_{14}H_{22}O_2Na$
		243.13	$C_{14}H_{20}O_2Na$
16	183.10, $C_8H_{16}O_3Na$	181.08	$C_8H_{14}O_3Na$
17	165.09, $C_8H_{14}O_2Na$	149.09	$C_8H_{14}ONa$

Table S2: FTIR Peak Assignments in the Frequency Range from 1200 to 4000 cm^{-1} of Adsorbed MEK on Hydroxylated and Deuteroxylated α-Fe_2O_3 Surfaces.[1,3–8]

Vibrational Mode	**Peak Assignment**	
	Hydroxylated - α-Fe_2O_3	**Deuteroxylated – α-Fe_2O_3**
Loss of surface O-H groups	3670, 3620	--
Appearance of surface O-H groups, H-bond networks	--	3617, 3458
C-H bond stretching vibrations	2971, 2941, 2910, 2883, 2855	3011, 2978, 2943, 2889
Loss of surface O-D groups	--	2078, 2672
Appearance of O-D, D-bond networks	--	2594, 2564, 2531
C-D bond stretching vibrations	--	2531, 2255, 2227, 2119
C=O bond stretching	1683	1683
Adsorbed water, bending vibration	1635	--
C=C bond stretching of an alpha-beta unsaturated ketone, other conjugated systems	1615, 1568	1593, 1569
C-H bond bending vibrations	1464, 1410, 1381, 1367, 1340	1492, 1474, 1463, 1411, 1385, 1359
C-O bond stretching vibrations, particularly of alcohols	1281, 1242, 1202, 1175	1280, 1209, 1170

Table S3: Major deuterated isotopes of MEK oligomers and their fragments observed upon exposure of MEK to deuteroxylated α-Fe_2O_3 and TiO_2 surfaces.

Oligomer	*m/z*	Observed Formula	Molecular Formula	Corresponding Non-Deuterated Compound/ Fragment	Identified on α-Fe_2O_3	Identified on TiO_2
Group A (MEK Dimer)	167.10	$C_8H_{16}O_2Na$	$C_8H_{16}O_2$	Compound 1	--[a]	√
	168.11	$C_8H_{15}DO_2Na$	$C_8H_{15}DO_2$	$C_8H_{16}O_2$ (Compound 1)	√	√
	169.12	$C_8H_{14}D_2O_2Na$	$C_8H_{14}D_2O_2$		√	√
	170.12	$C_8H_{13}D_3O_2Na$	$C_8H_{13}D_3O_2$		√	√
	171.13	$C_8H_{12}D_4O_2Na$	$C_8H_{12}D_4O_2$		√	√
	172.14	$C_8H_{11}D_5O_2Na$	$C_8H_{11}D_5O_2$		√	√[c]
	173.14	$C_8H_{10}D_6O_2Na$	$C_8H_{10}D_6O_2$		√	√
	174.15	$C_8H_9D_7O_2Na$	$C_8H_9D_7O_2$		√[b]	√
	175.15	$C_8H_8D_8O_2Na$	$C_8H_8D_8O_2$		√	√
	176.16	$C_8H_7D_9O_2Na$	$C_8H_7D_9O_2$		√	√
Group B (MEK Trimer)	221.15	$C_{12}H_{22}O_2Na$	$C_{12}H_{22}O_2$	Compound 3	--	√
	223.16	$C_{12}H_{20}D_2O_2Na$	$C_{12}H_{20}D_2O_2$	$C_{12}H_{22}O_2$ (Compound 3)	--	√
	224.17	$C_{12}H_{19}D_3O_2Na$	$C_{12}H_{19}D_3O_2$		--	√
	225.18	$C_{12}H_{18}D_4O_2Na$	$C_{12}H_{18}D_4O_2$		--	√
	226.18	$C_{12}H_{17}D_5O_2Na$	$C_{12}H_{17}D_5O_2$		--	√
	227.19[d]	$C_{12}H_{16}D_6O_2Na$	$C_{12}H_{16}D_6O_2$		--	√
	228.19[e]	$C_{12}H_{15}D_7O_2Na$	$C_{12}H_{15}D_7O_2$		--	√[c]
	229.20[f]	$C_{12}H_{14}D_8O_2Na$	$C_{12}H_{14}D_8O_2$		--	√
	230.21	$C_{12}H_{13}D_9O_2Na$	$C_{12}H_{13}D_9O_2$		--	√
	231.21[g]	$C_{12}H_{12}D_{10}O_2Na$	$C_{12}H_{12}D_{10}O_2$		--	√
	227.19[d]	$C_{12}H_{12}D_8O_2Na$	$C_{12}H_{12}D_8O_2$	$C_{12}H_{20}O_2$ (Compound 3 – 2H)	√	--
	228.19[e]	$C_{12}H_{11}D_9O_2Na$	$C_{12}H_{11}D_9O_2$		√	√
	229.20[f]	$C_{12}H_{10}D_{10}O_2Na$	$C_{12}H_{10}D_{10}O_2$		√[b]	√
	230.20	$C_{12}H_9D_{11}O_2Na$	$C_{12}H_9D_{11}O_2$		√	√
	231.21[g]	$C_{12}H_{12}D_{10}O_2Na$	$C_{12}H_{12}D_{10}O_2$	$C_{12}H_{22}O_2$ (Compound 3)	√	√
	232.22	$C_{12}H_{11}D_{11}O_2Na$	$C_{12}H_{11}D_{11}O_2$		√	√
	233.23	$C_{12}H_{10}D_{12}O_2Na$	$C_{12}H_{10}D_{12}O_2$		√	√
Group C (MEK Tetramer)	281.24	$C_{16}H_{22}D_6O_2Na$	$C_{16}H_{22}D_6O_2$	$C_{16}H_{28}O_2$ (Compound 7)	--	√
	282.24	$C_{16}H_{21}D_7O_2Na$	$C_{16}H_{21}D_7O_2$		--	√
	283.24	$C_{16}H_{20}D_8O_2Na$	$C_{16}H_{20}D_8O_2$		--	√
	284.25[h]	$C_{16}H_{19}D_9O_2Na$	$C_{16}H_{19}D_9O_2$		--	√
	285.26[i]	$C_{16}H_{18}D_{10}O_2Na$	$C_{16}H_{18}D_{10}O_2$		--	√
	286.27	$C_{16}H_{17}D_{11}O_2Na$	$C_{16}H_{17}D_{11}O_2$		--	√
	287.27[j]	$C_{16}H_{16}D_{12}O_2Na$	$C_{16}H_{16}D_{12}O_2$		--	√

	283.25	$C_{16}H_{16}D_{10}O_2Na$	$C_{16}H_{16}D_{10}O_2$	$C_{16}H_{26}O_2$ (Compound 4 – 2H)	√	√
	284.25 [h]	$C_{16}H_{15}D_{11}O_2Na$	$C_{16}H_{15}D_{11}O_2$		√	√
	285.26 [i]	$C_{16}H_{14}D_{12}O_2Na$	$C_{16}H_{14}D_{12}O_2$		√	√
	286.26	$C_{16}H_{13}D_{13}O_2Na$	$C_{16}H_{13}D_{13}O_2$		√ [b]	√
	287.27 [j]	$C_{16}H_{12}D_{14}O_2Na$	$C_{16}H_{12}D_{14}O_2$		√	√
	288.28	$C_{16}H_{11}D_{15}O_2Na$	$C_{16}H_{11}D_{15}O_2$		√	--
	289.29	$C_{16}H_{14}D_{14}O_2Na$	$C_{16}H_{14}D_{14}O_2$	$C_{16}H_{28}O_2$ (Compound 4)	√	--
	290.29	$C_{16}H_{13}D_{15}O_2Na$	$C_{16}H_{13}D_{15}O_2$		√	--
	299.24	$C_{16}H_{12}D_{12}O_3Na$	$C_{16}H_{12}D_{12}O_3$	$C_{16}H_{24}O_3$ (Compound 6 – 6H)	√	--
	302.14	$C_{16}H_{17}D_3O_4Na$	$C_{16}H_{17}D_3O_4$	$C_{16}H_{32}O_4$ (Compound 5 – 12H)	--	√ [c]
	303.27	$C_{16}H_{16}D_{12}O_3Na$	$C_{16}H_{16}D_{12}O_3$	$C_{16}H_{28}O_3$ (Compound 6 – 2H)	√	--

a: Not observed, *b*: Observed with highest intensity for corresponding oligomer group on α-Fe_2O_3 surfaces, *c*: Observed with highest intensity for corresponding oligomer group on TiO_2 surfaces, *d* - *j*: These *m/z* pairs differ in their 3rd or 4th decimal value thus resulting different H:D ratio in their corresponding observed formulae.

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