Supplementary Information for

First principles mechanistic study of self-limiting oxidative adsorption of remote oxygen plasma during the atomic layer deposition of alumina

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These supplementary figures show initial geometries prior to DFT optimization, generated by introducing various concentrations of singlet oxygen atoms to the MS model of the methylated surface.

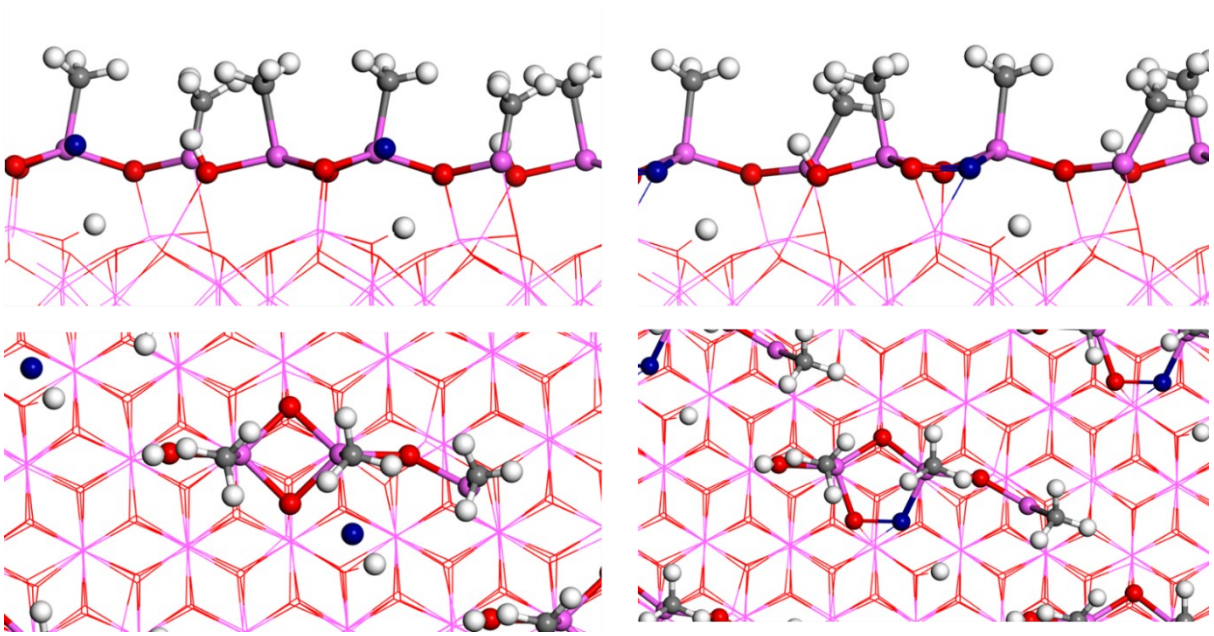

Figure A1: Side and top views showing how a single ^{1}O atom attacks a 4-coordinated surface aluminium atom before relaxation (left panel) and after relaxation (right panel). After relaxation, there is no insertion of ^{1}O into Al-C, rather forming adsorbed peroxide *i.e.* $(O_2)^{2-}$ with computed O-O bond length = 1.53 Å.

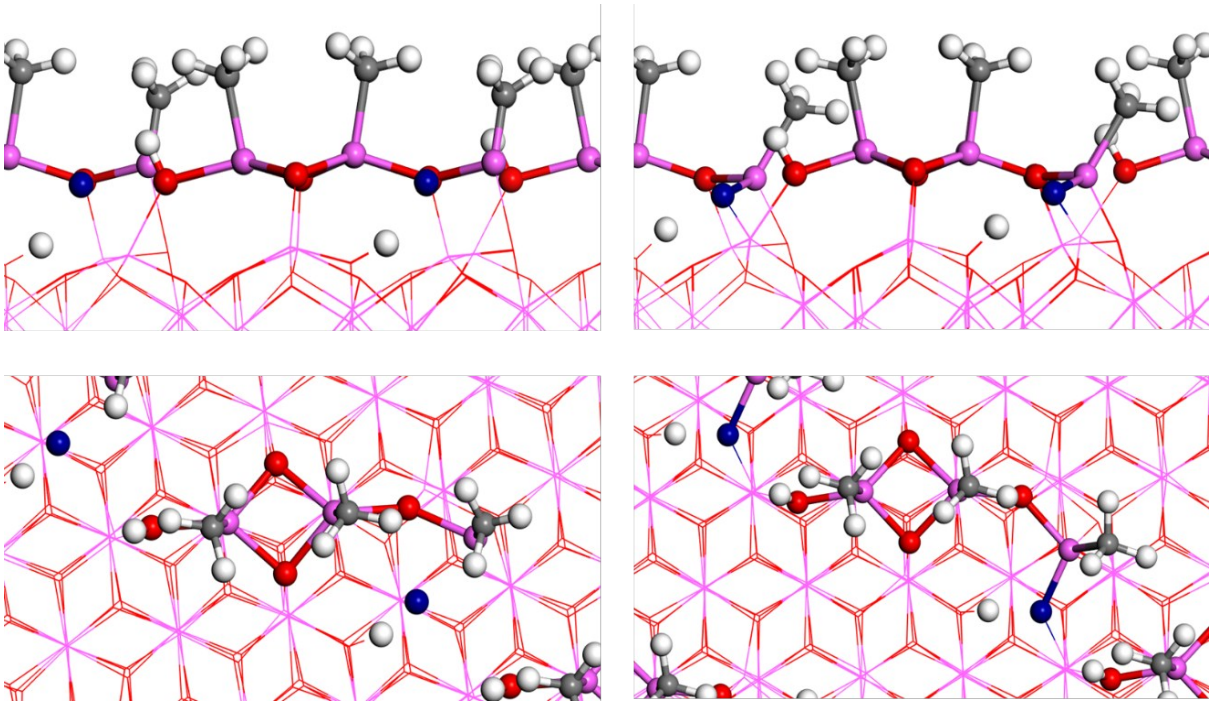

Figure A2: Side and top views showing how a single ^{1}O atom attacks a 4-coordinated surface aluminium atom before relaxation (left panel) and after relaxation (right panel). After relaxation, there is no insertion of ^{1}O into Al-C, rather forming a bridged to Al in the bulk (Al-O-Al).

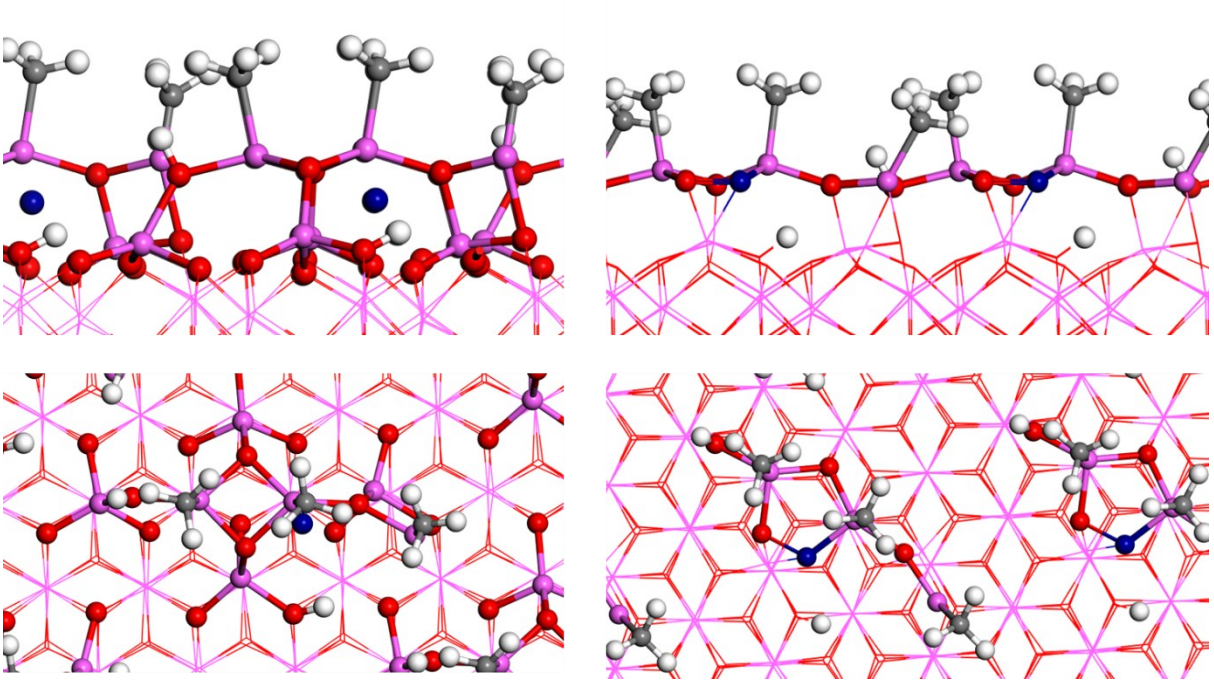

Figure A3: Side and top views showing how a single ^{1}O atom reacts in the subsurface before relaxation (left panel) and after relaxation (right panel). After relaxation, ^{1}O forms a peroxide with a surface oxygen with computed O-O bond length = 1.53 Å.

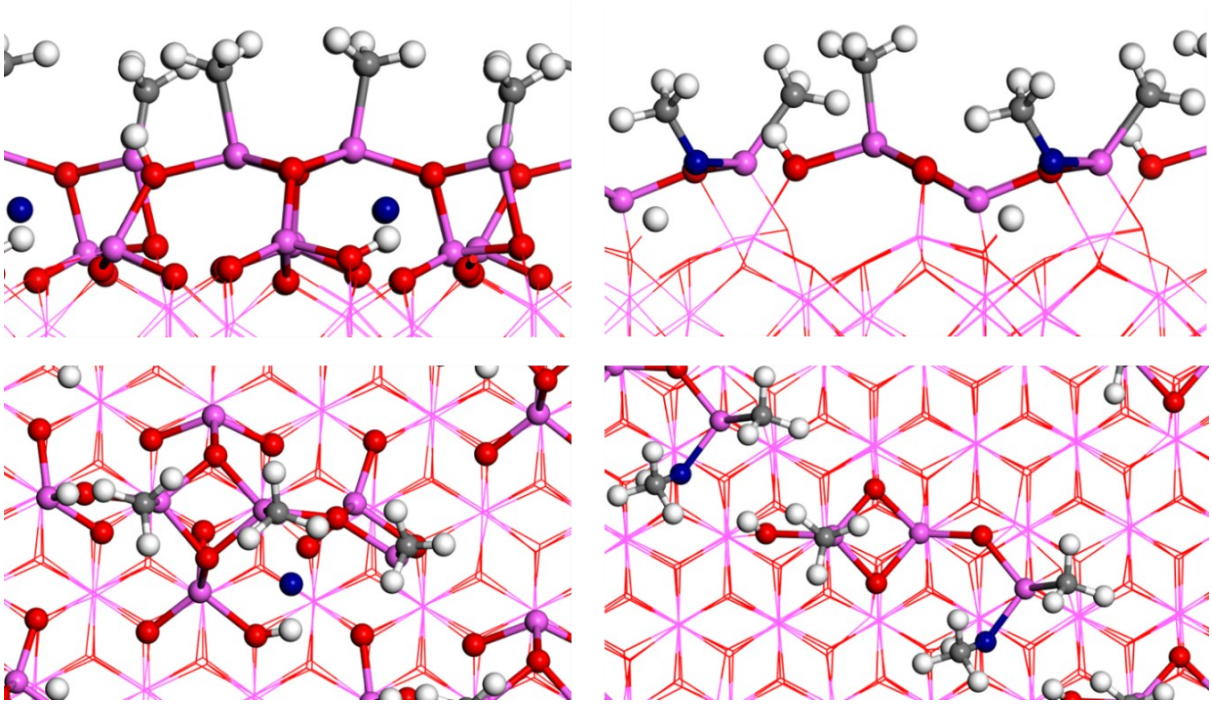

Figure A4: Side and top views showing how a single ^{1}O atom reacts in the subsurface before relaxation (left panel) and after relaxation (right panel). After relaxation, ^{1}O inserts between Al-C bond to form $–OCH_3$, as in reaction D.

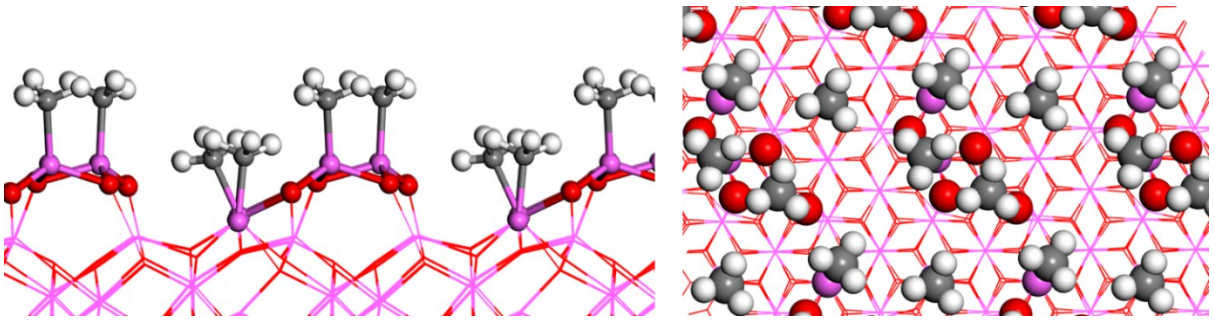

Figure B1: Side and top view of the four $AlCH_3$ fragments on the surface after the adsorption of 4 TMA with subsequent desorption of 8 CH_4. This geometry is used for relaxation in reaction B^*, Table 1.

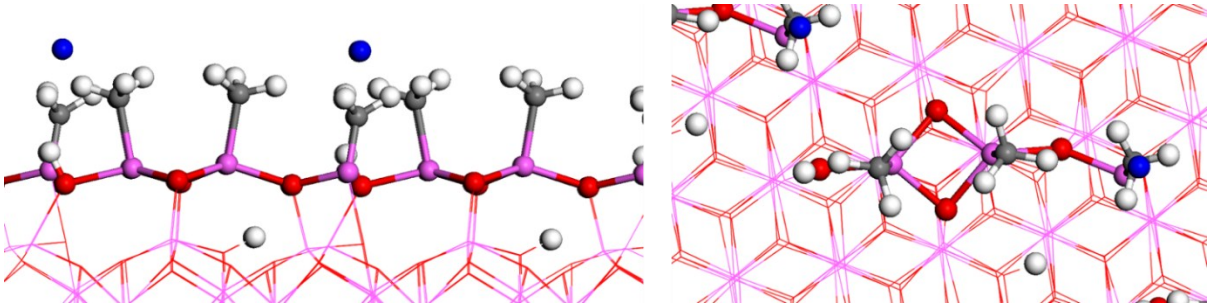

Figure C1: Side (left panel) and top (right panel) views prior to relaxation of a single ^{1}O approaching the carbon atom of the methyl ligand from the top. This geometry is used for relaxation in reaction C, Table 2.

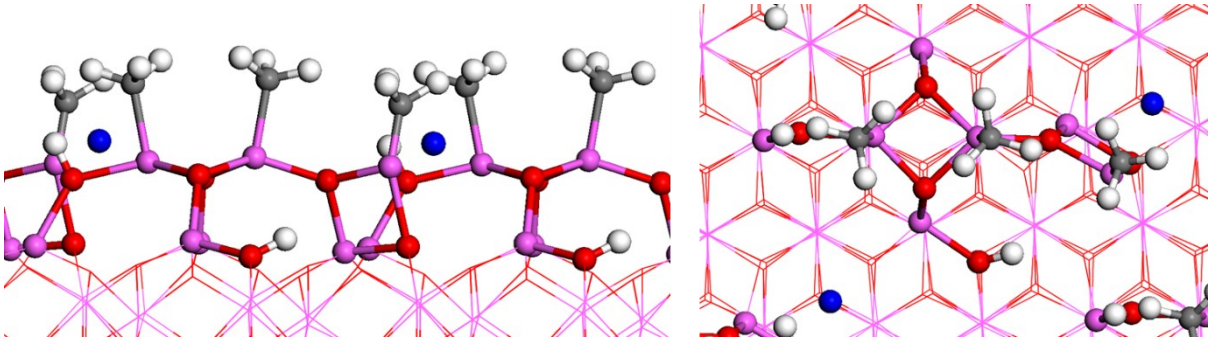

Figure D1: Side (left panel) and top (right panel) views prior to relaxation of a single ^{1}O approaching a surface aluminium atom from the side. This geometry is used for relaxation in reaction D, Table 2.

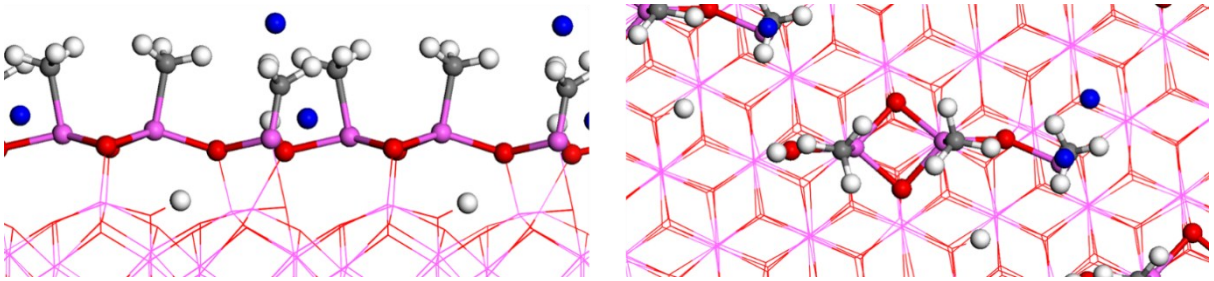

Figure E1: Side (left panel) and top (right panel) views of surface models of oxidation of MS with two ^{1}O prior to relaxation. This geometry is used for relaxation in reaction E, Table 2.

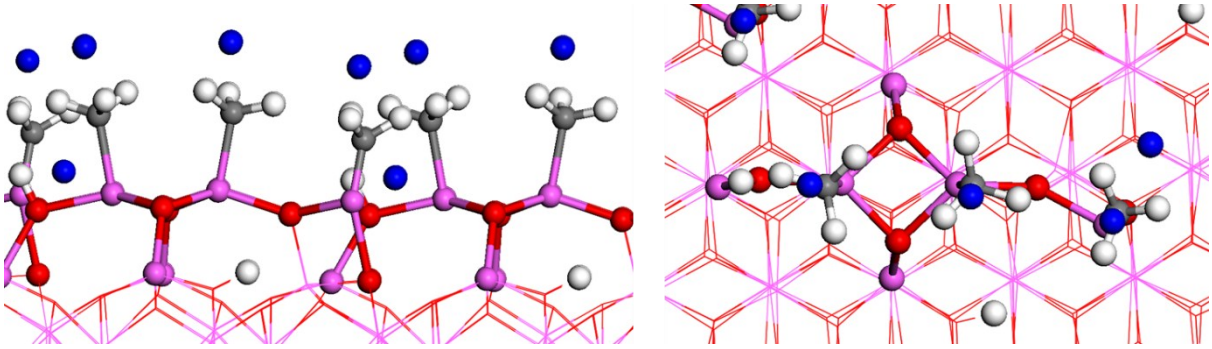

Figure F1: Side (left panel) and top (right panel) views of surface models of oxidation of MS with four ^{1}O prior to relaxation. Three of these ^{1}O atoms attack the ligand from the top while the remaining one attacks surface aluminium from the side. This geometry is used for relaxation in reaction F, Table 2.

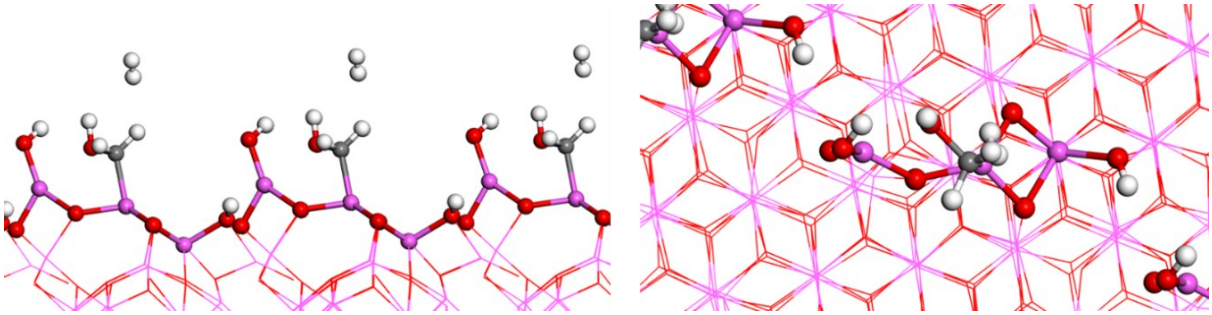

Figure F2: Short DFT-based MD simulations from the same initial geometry as F at 423 K spontaneously produced the same by-products and surface fragments. However, H^- that was weakly bonded to Al in reaction F, Table 2, combined with a nearby proton in the subsurface layer to produce H_2, as shown here in the final geometry from the MD simulation.

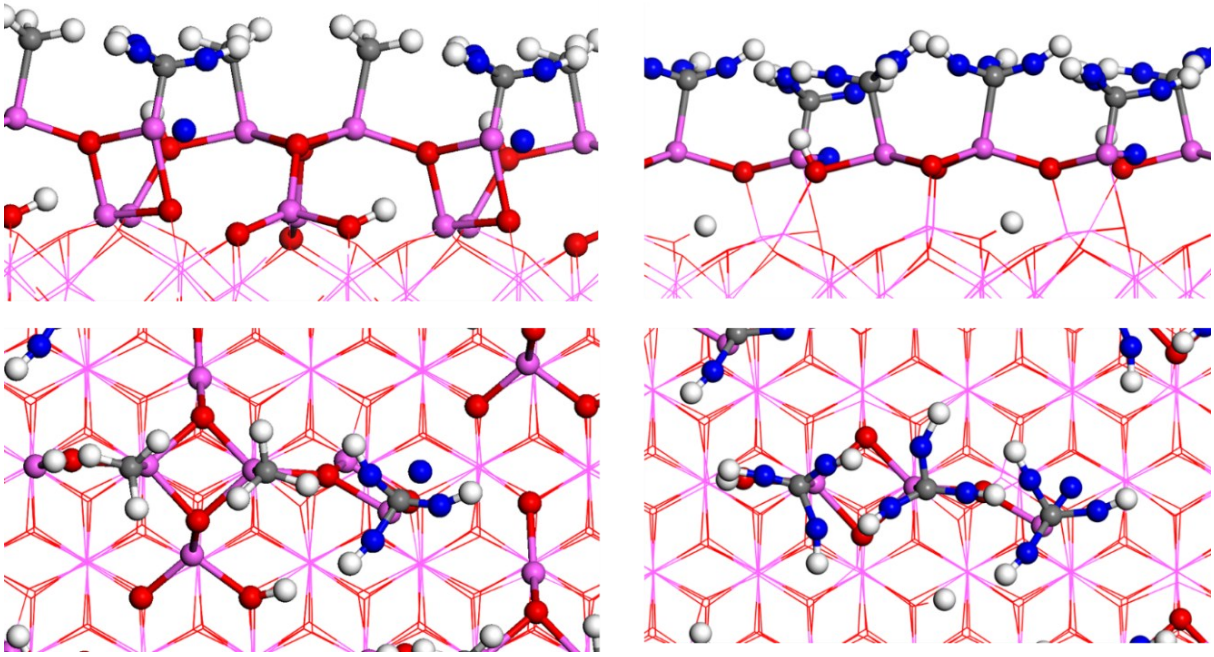

Figure H1: Side and top views of surface before geometry optimisation of MS with three ^{1}O atoms (left panel) and nine ^{1}O atoms (right panel) inserted into multiple C-H bonds. These geometries are used respectively for relaxation in reaction H and O, Table 2.

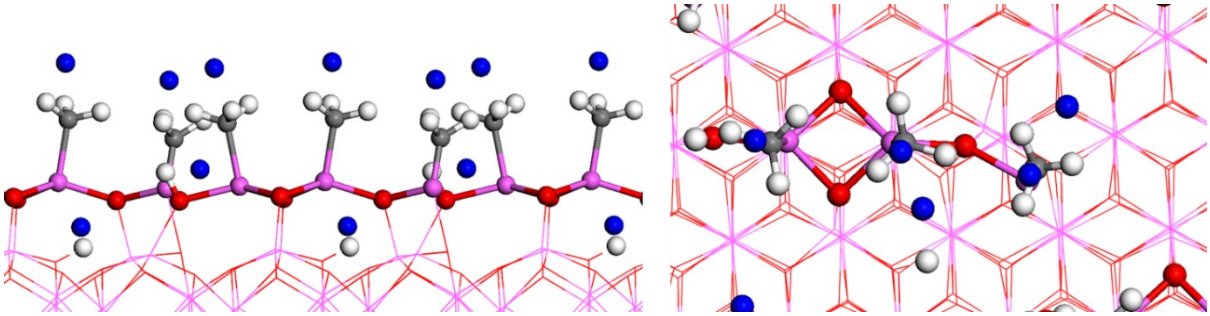

Figure I1: Side (left panel) and top (right panel) views of surface models of oxidation of MS with five ^{1}O prior to relaxation. This geometry is used for relaxation in reaction I, Table 2.

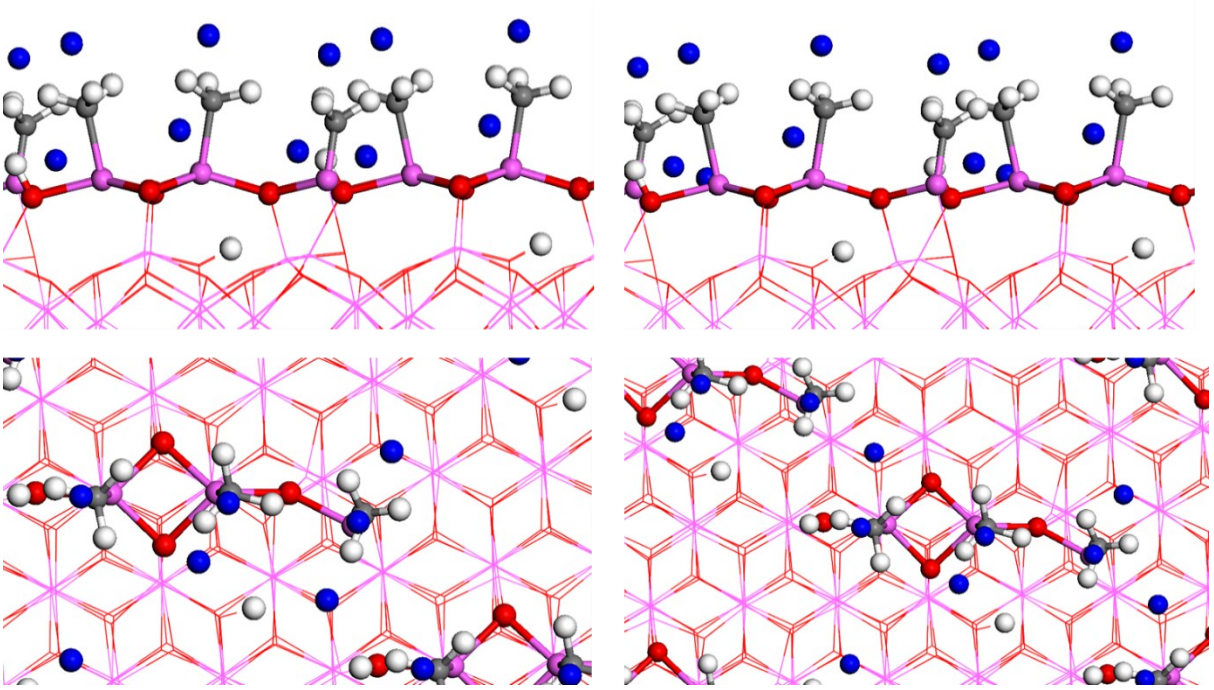

Figure J1: Side and top views of two surface before geometry optimisation of MS with six ^{1}O atoms in different positions. After relaxation, CH_3OH (left panel) while two CH_2O (right panel) were produced spontaneously. The structure in the right was used as the initial geometry to determine the total reaction energy, generating 3OH groups on the surface as seen in Figure G.

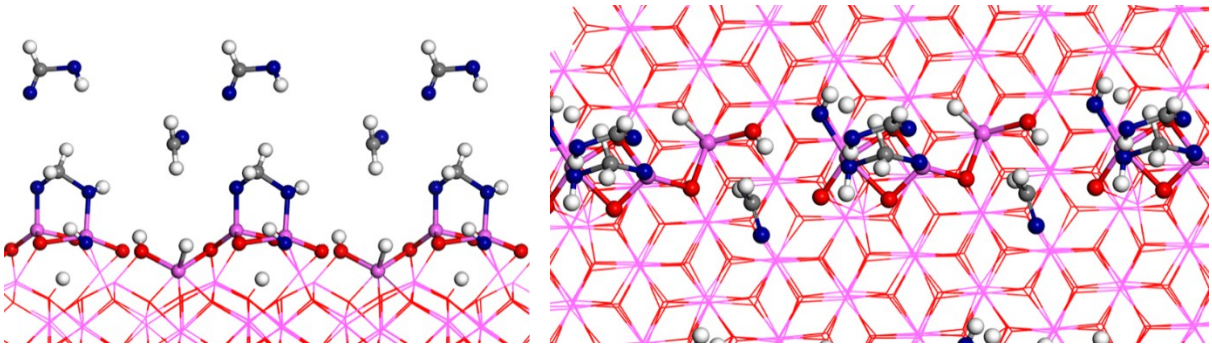

Figure J2: Side (left panel) and top (right panel) views of surface after short DFT-MD runs. The initial geometry in structure J1 (left panel) was used for this run producing CH_2O and HCOOH as by-products.

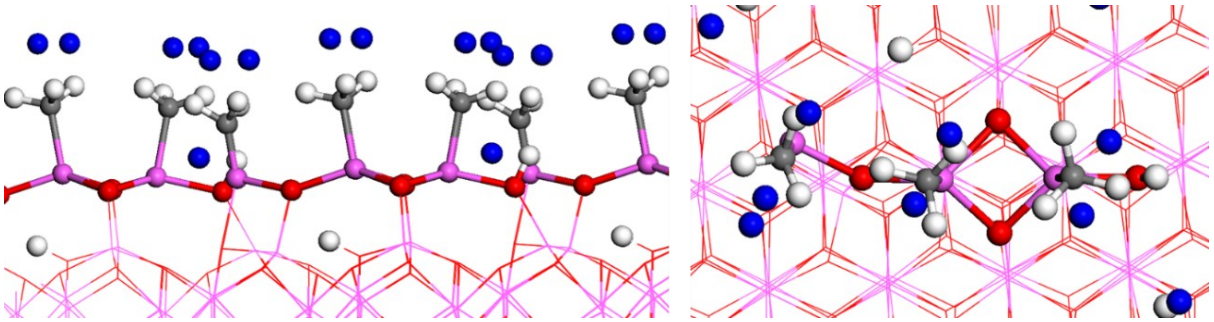

Figure L1: Side (left panel) and top (right panel) views of surface models of oxidation of MS with seven ^{1}O prior to relaxation. This geometry is used for relaxation in reaction L, Table 2.

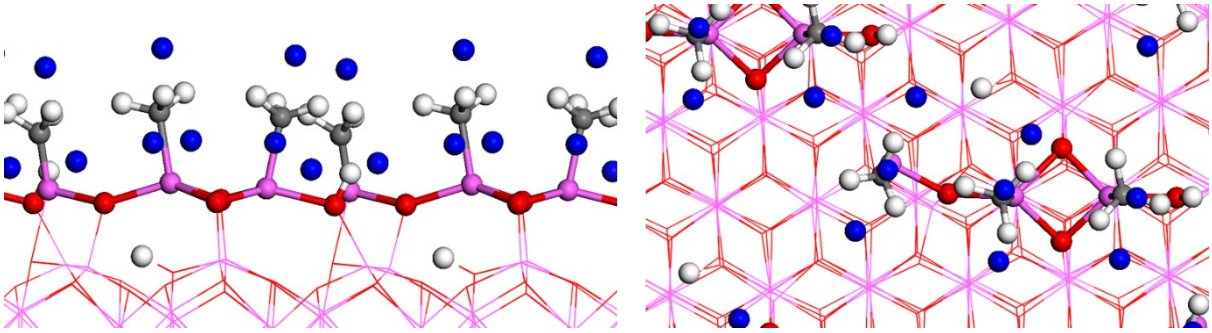

Figure M1: Side (left panel) and top (right panel) views of surface models of oxidation of MS with eight ^{1}O prior to relaxation. This geometry is used for relaxation in reaction M, Table 2.