Electronic Supplementary Material (ESI) for Faraday Discussions.

Supplementary Information

A QM/MM based approach to radical mechanism of the catalytic production of methanol from glycerol.

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S1 Calculation of the optimised cell volume

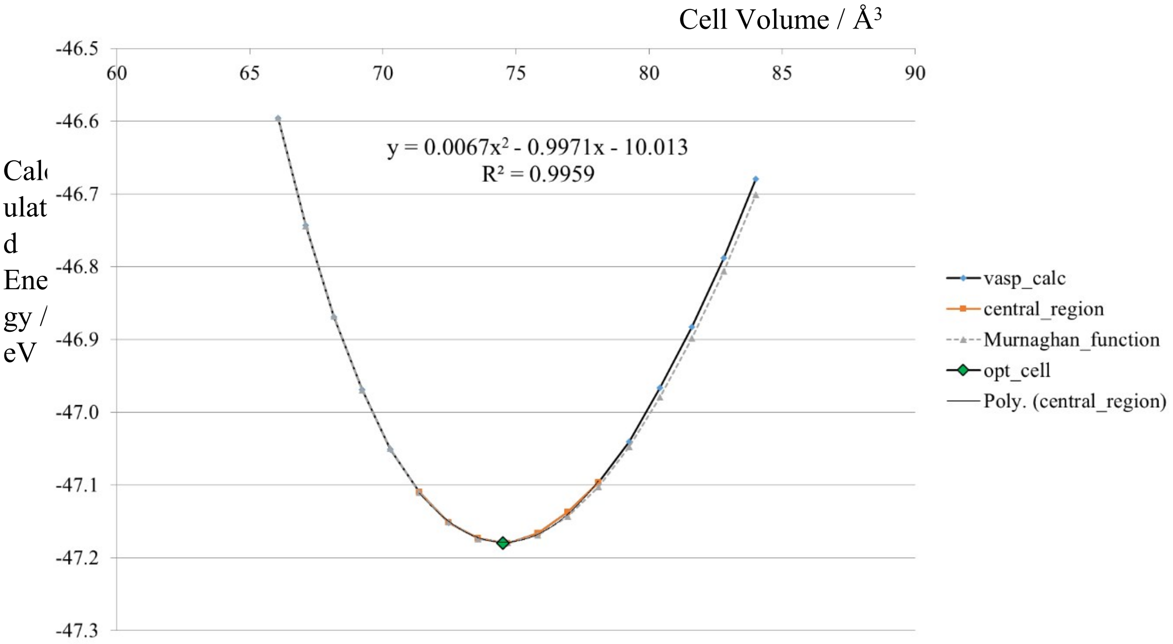

Figure S1: Plot of calculated energy against cell volume for MgO using the face centred cell with stoichiometry Mg_4O_4. VASP calculation, PBEsol functional, planewave cut off 800 eV, *k*-point sampling 5×5×5.

Figure S1 shows the total calculated cell energy for the MgO face centred cubic unit cell as a function of the cell volume. The cell volume was varied by a series of scaling factors from -4% to +4% with reference to the experimentally reported cell dimensions in 0.5% steps. Near to the minimum the curve is roughly parabolic and so a simple quadratic fit can be used to estimate the minimum cell energy, the corresponding cell volume and the bulk modulus from the curvature of the quadratic. These were used as inputs to a numerical sum of squares fitting routine which minimised the difference between the calculated data across the whole range of volumes and the Murnagahan equation of state:

$$E = E_0 + \frac{B_0 V}{B_0^{'}}\left(\frac{\left(\frac{V_0}{V}\right)^{B_0^{'}}}{B_0^{'} - 1} + 1\right) - \frac{V_0 B_0}{\left(B_0^{'} - 1\right)} \tag{S1}$$

with,

$$B_0' = \left(\frac{\partial B_0}{\partial p}\right)_T \tag{S2}$$

Here E is the energy from the Murnagahan function and E_0 the mimimum energy value. B_0 is the bulk modulus and $B_0^{'}$ its derivative with respect to pressure, p, at constant temperature, T. V is the system volume and V_0 the volume at the energy minimum. The variable parameters in the curve fitting routine are E_0, V_0, B_0 and $B_0^{'}$. Initial estimates for the E_0, V_0, B_0 where taken from the quadratic curve fit to the central region and a starting value of 4 for the $B_0^{'}$ parameter was also employed.

Based on the fitted minimum cell volume an optimum scaling factor was estimated and a final vasp bulk calculation gave the cell energy indicated by the green diamond at the minimum in the plot of Figure 1. This scale factor was 0.9992 % and the resulting cell was used as the basis from which to cut simulation slabs for the surface calculations.

S2 Calculation of surface energy for periodic slab models

The calculations based on periodic slab models were based on a 5 layer slab with a supercell expansion of the MgO(100) surface of 2×2 with a 15 Å vacuum gap included to separate unit periodic images of slabs in the direction perpendicular to the surface. This resulted in a surface model with stoichiometry $Mg_{40}O_{40}$ and dimensions a=b= 8.4138 Å and c= 23.4138 Å. For consistency with the QM/MM calculations the upper 4 layers of the slab were optimised with only the lowest layer held fixed at the bulk ion positions. This means that the two faces of the slab become inequivalent on optimisation and so to calculate the surface energy of the system the following expression was used:

$$E^{opt}_{S} = \frac{E_{slab} - nE_{bulk}}{S} - E^{term}_{S} \tag{S3}$$

where E_{slab} is the energy of the optimised slab with the lowest layer ions constrained. E_{bulk} is the optimised energy of the bulk reference calculation and the factor n accounts for the difference in stoichiometry of the slab and the bulk. Here the slab has the formula $Mg_{40}O_{40}$ whereas the bulk calculation is performed with a cell stoichiometry of Mg_4O_4 and so n=10. E^{term}_{S} takes account of the lower surface being held at the bulk termination and so is the surface energy calculated for the slab when both faces are held at the bulk termination geometry:

$$E^{term}_{S} = \frac{E^{term}_{slab} - nE_{bulk}}{2S} \tag{S4}$$

now E_{slab}^{term} is the slab energy with all ions at their bulk positions. At the PBEsol level we find E_{slab}^{term}=1.086 J m^{-2} and E_{slab}^{opt}=1.065 J m^{-2} while PBEsol+D3 calculations yield E_{slab}^{term}=1.500 J m^{-2} and E_{slab}^{opt}=1.467 J m^{-2}. The higher surface energy with the dispersion correction would be expected as the ions in the bulk will have more interactions with neighbours than those in the surface and as dispersion is an attractive force the energy to form the surface is increased when it is included.

S3 Convergence of adsorption energy with slab area in periodic DFT calculations

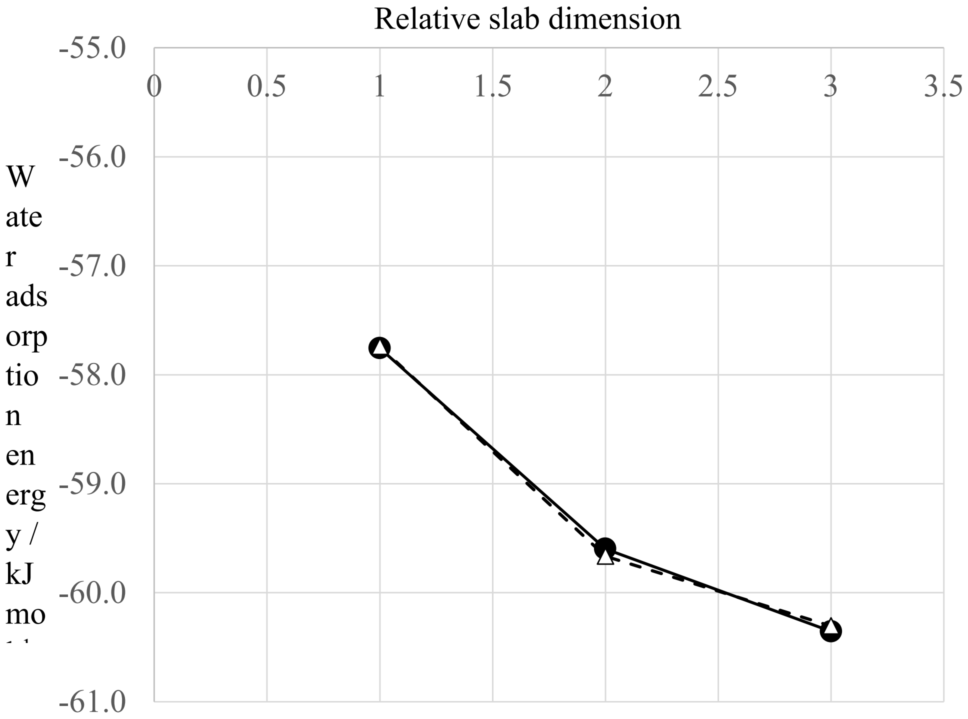

Figure S2. Calculated adsorption energy of water as a function of slab surface area (filled circles, solid lines) and fitted dependence according to equation S5 (white triangles, dashed lines). Calculations carried out with VASP and the PBEsol functional, planewave cut-off 800 eV, k-point sampling 3×3×1. Slab dimension refers to the relative length of the side of the square surface repeat unit relative to the 1×1 surface which has a surface area of 17.70 Å^2.

In this set of calculations we have tested the adsorption energy, E_{ads}, of water to the MgO(001) surface as a function of the surface area of the MgO slab model used in a periodic DFT calculation with the PBEsol functional. Figure S2 shows the calculated adsorption energy as a function of the relative slab dimension for calculations on the face centred cubic (001) cell (containing 2 Mg^{2+} and 2 O^{2-} in the surface layer), a 2×2 and a 3×3 surface expansion. The distance between the adsorbate increases in proportion to the relative slab dimension.

To estimate the effective infinite dilution value, E^{∞}_{ads}, extrapolation of the data was attempted by fitting functions of the type:

$$E_{ads} = E^{\infty}_{ads} + \frac{a}{r^n} \tag{S5}$$

where a and E^{∞}_{ads} were fitting variables and r the slab dimension variable. Various exponents, n, were tested and we found that only values of $n \leq 1$ gave sum of squares values less than 10^{-2}, with n=1 giving $E^{\infty}_{ads} = -61.6$ kJ mol^{-1}.

S3 Force field methodology for QM/MM calculations

The force field (FF) used in the molecular mechanics (MM) regions of our QM/MM calculations consists of Buckingham potentials between Mg^{2+} and O^{2-} ions, as well as between different O^{2-} ions. Additionally, the O^{2-} ions are split into a core (O_{co}) and shell (O_{sh}), bound by a harmonic potential, to allow polarisability. Buckingham potentials are calculated using the shell co-ordinates. The potentials were based on those defined by Catlow and co-workers[1] but modified to match the structural and dielectric properties of MgO predicted by periodic calculations using the PBE0 functional and 'tight' basis sets with FHI-aims. Using a FF in the MM region which matches as closely as possible the structural and dielectric properties of the QM region minimises force imbalances at the boundary between the two regions. The potential parameters used in this work are summarised in Table S1.

The harmonic potential, E_{co-sh}^{harm}, linking oxygen core and shell co-ordinates has the form:

$$E_{co-sh}^{harm} = k_2 {d_{co-sh}}^2 \qquad \text{(S6)}$$

Where k_2 is the core-shell spring constant, given in Table 1 and d_{co-sh} is the displacement of the core/shell co-ordinates.

The Buckingham potential energy, E_{ij}^{Buck}, between centres i and j is calculated using,

$$E_{ij}^{Buck} = A_{ij} e^{-r_{ij}/\rho_{ij}} - \frac{C_{ij}}{{r_{ij}}^6} \qquad \text{(S7)}$$

Where the potential parameters, A_{ij}, ρ_{ij} and C_{ij} depend on the type of interaction centres that are being considered (Mg_{co}, O_{co} and O_{sh}) and r_{ij} is their separation. The Buckingham potential contribution to the MM energy is summed within a cut-off distance with the values used for parameters and cut-offs given in Table S1.

Table S1. Force Field Parameters used in this work.[1]

Coulomb and Harmonic	q_{co} / |e|	q_{sh} / |e|	k_2 / eV Å^{-2}	
Mg_{co}	+2.00	n/a	n/a	
O_{co}/O_{sh}	+0.871381	-2.871381	57.015077	
Buckingham	**A / eV Å^{-2}**	**ρ / Å**	**C / eV Å^{6}**	**Cutoff / Å**
$Mg_{co} - O_{sh}$	1448.73348	0.294799	0.00	10.00
$O_{sh} - O_{sh}$	22764.00873	0.149	27.781268	12.00

S4 Calculations for experimental data

Equation S8 was used to calculate the glycerol conversion (C_{GLY}) based on the molar difference between carbon from glycerol fed into the reactor, g_{mi}, and that detected at the outlet, g_{mo}:

$$C_{GLY}\,(\%) = \left(\frac{g_{mi} - g_{mo}}{g_{mi}}\right) \times 100 \tag{S8}$$

The product selectivity ($S_p(x)$, carbon *mol.* %) for any product, x, was calculated from the moles of carbon recovered in x, x_{Cm} divided by the sum of moles of carbon in each product, y_{Cm} (eq. S9).

$$S_p(x)(\%) = \left(\frac{x_{Cm}}{\sum_y y_{Cm}}\right) \times 100 \tag{S9}$$

The carbon balance can be obtained by comparing the moles of carbon accounted for in unreacted glycerol and in the identified products to the moles of carbon in glycerol entering the reactor:

$$B_C(\%) = \left(\frac{g_{mo} + \sum_x x_{Cm}}{g_{mi}}\right) \times 100 \tag{S10}$$

Functional group yield (Y, carbon *mol.* %) data were calculated by the sum of the selectivities for products containing that functional group S_G, multiplied by conversion C_{GLY}, multiplied by the carbon balance B_C, excluding coke (eq. S11).

$$Y\,(\%) = \left(\frac{(\Sigma\, S_G)\; x\; C_{GLY}}{100}\right) \times B_C\,(\%) \tag{S11}$$

The overall carbon balance B_{Ctot} was calculated (eq. S12) by dividing the sum of the carbon moles of products x_{Cm}, coke x_{Ccoke} estimated from post reaction characterisation and unreacted glycerol g_{mo} by the carbon moles of glycerol injected into the reactor g_{mi}.

$$B_{Ctot} = \left(\frac{\sum_x x_{Cm} + x_{Ccoke} + g_{mo}}{g_{mi}}\right) \times 100 \tag{S12}$$

The hydrogen balance B_H was calculated (eq. S13) by dividing the sum of the hydrogen moles of products x_H, including the water product estimated from elementary reaction steps, hydrogen gas (GC2) x_{Hgas} and moles of hydrogen in unreacted glycerol g_{Hmo} by the moles of hydrogen in glycerol injected into the reactor g_{Hmi}.

$$B_H = \left(\frac{x_{Hp} + x_{Hgas} + g_{Hmo}}{g_{Hmi}}\right) \times 100 \tag{S13}$$

The methanol space-time-yield STY_{MEOH}, was calculated (eq. S14) from the mass of methanol m_{MEOH}, produced per h (reaction time Rt), per mass of catalyst (m_{cat}, kg).

$$STY_{MEOH} = \left(\frac{m_{MEOH}\,(g)}{Rt\,(h)\,\times\,m_{cat}\,(kg)}\right) \tag{S14}$$

S4 Experimental selectivity to identified products

Table S2

	Catalyst material[a]		
	MgO_(450)	MgO_(650)	MgO_(750)
product	Sel.[b] / %	Sel.[b] / %	Sel.[b] / %
acetaldehyde	7.2	7.0	6.2
propionaldehyde	0.2	0.0	0.1
acetone	0.1	0.1	0.1
acrolein	13.8	12.6	11.1
butyraldehyde	0.0	0.0	0.0
methanol	8.6	8.1	8.0
2-propanol	0.0	0.0	0.0
ethanol	0.3	0.3	0.3
2,3-butanedione	0.1	0.1	0.1
2-butanol	0.0	0.0	0.0
1-propanol	0.1	0.0	0.0
3-hexanone	0.0	0.0	0.0
2-hexanone	0.0	0.0	0.0
2-methyl-1-propanol	0.0	0.0	0.0
allyl alcohol	0.8	0.6	0.6
cyclopentanone	0.1	0.1	0.1
hydroxyacetone	26.9	26.0	22.2
3-ethoxy-1-propanol	3.9	2.1	1.7
acetic acid	0.3	0.2	0.2
Glycidol	0.0	0.1	0.7
propionic acid	4.6	2.6	3.1
1,2-propanediol	2.8	2.7	2.4
unknown(s)	12.1	20.3	28.1
ethylene glycol	14.0	14.5	13.4
1,3-propanediol	2.3	0.8	0.2
phenol	0.3	0.0	0.2
CO	0.4	0.6	0.3
CO_2	0.9	0.5	0.0
Glycerol conversion	8	5	7
Carbon balance	105	102	100
MeOH S.T.Y.	21	32	32

Notes: *a*) Number in brackets refers to the temperature (°C) of the calcination step in the catalyst preparation. *b*) Selectivity defined in terms of moles of carbon in products detected, see equation S9.

References

1. G. V. Lewis and C. R. A. Catlow, Potential models for ionic oxides, *J. Phys. C Solid State Phys.*, 1985, **18**, 1149–1161.