Substrate–Solvent Crosstalk—Effects on Reaction Kinetics and Product Selectivity in Olefin Oxidation Catalysis

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Experimental procedures

General

All reagents were purchased from Aldrich and used as supplied.

FTIR spectra were measured with a Nicolet Nexus 6700 FTIR spectrometer using Diffuse Reflectance accessory for clay materials. All FTIR spectra were measured in the 400-4000 cm^{-1} range and using 4 cm^{-1} resolution. Powder XRD measurements were taken on a Philips Analytical PW 3050/60 X'Pert PRO (theta/2 theta) equipped with X'Celerator detector and with automatic data acquisition (X'Pert Data Collector (v2.0b) software), using monochromatized Cu-Kα radiation as incident beam, 40 kV–30 mA. UV/Vis spectra were measured on a Shimadzu UV2450 in the 400-700 nm range equipped with a Peltier cell for temperature control. Diffuse reflectance UV/Vis (DRUV) measurements were accomplished using the same spectrophotometer equipped with an integrating sphere in the 400-700 nm range, using BaSO$_4$ as reference material.

TGA studies were performed using a Perkin-Elmer TGA7 thermobalance system at a heating rate of 10 K·min^{-1} under N$_2$. Microanalyses were performed at the University of Vigo.

Small angle neutron diffraction experiments

All neutron diffraction data were collected at the ISIS pulsed neutron and muon source at the Rutherford Appleton Laboratory, UK, using the Small Angle Neutron Diffractometer for Amorphous and Liquid Samples (SANDALS) instrument [S1].

All experiments were carried out measuring the neat components using the isotopic substitution method, Table S1, taking full advantage of the isotopic contrast between hydrogen and deuterium. Mixtures of the solvents (acetonitrile and toluene) and styrene replicating the mol ratios in a catalytic experiment were measured as well.

Table S1. Isotopic substitution scheme (*H* refers to fully protiated, *D* to fully deuterated and *HD* to equimolar mixture of both isotopomer compounds)

Styrene	Solvent
D	D
D	HD
D	H
HD	D
H	D

D	D
D	D
HD	HD

Samples were then loaded into null-scattering $Ti_{0.68}Zr_{0.32}$ flat cells with $35\times40\times1$ mm internal dimensions and wall thickness of 1 mm. Prior to the experiments, each empty sample cell, the empty diffractometer and a 3.0 mm thick vanadium standard sample were measured. During the measurements, the samples were maintained at a temperature of 298 K. Data were corrected for multiple scattering and absorption, being thereafter normalized to the incoherent scattering of vanadium using the Gudrun software[S2].

The corrected neutron diffraction data were then analyzed using the Empirical Potential Structure Refinement (EPSR) method, which allows the construction of three dimensional atomistic structural models of liquids or disordered samples that are consistent with experimental scattering data after which, the radial distribution functions were calculated[S3,S4].

MCM-41 synthesis

The MCM-41 type mesostructured silica material for the conversion of styrene oxide was prepared, according to the literature, using myristyltrimethylammonium bromide ($C_{14}TAB$) as surfactant [S5]. The batch was split into two sub-batches according to the template removal method; template removal was one by calcination (yielding MCM_C) or by washing with HCl-acidified methanol (yielding MCM_{AW}).

Characterization of the MCM_C and MCM_{AW} materials

Afterwards the synthesis batch was split into two sub-batches according to the template extraction procedure. One of the sub-batches was calcined (denoted MCM_C) while the other one was washed with HCl-acidified methanol (denoted MCM_{AW}) [S5].

Textural properties were assessed by powder XRD and sorption/desorption N_2 isotherms were also carried out for textural parameters estimation. All resulting materials were of good quality according to the X-ray diffraction (XRD) powder patterns (Fig. S1).
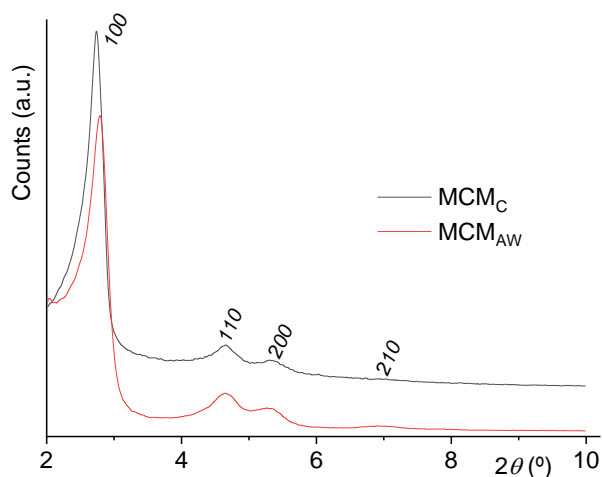
Figure S1. XRD powder patterns of MCM$_C$ and MCM$_{AW}$ materials (the diffractograms have been vertically shifted for clarity).

The XRD powder patterns (Fig. S1) of both MCM$_C$ and MCM$_{AW}$ pristine materials exhibited four reflections indexed to a hexagonal cell as (100), (110), (200) and (210) in the $2 < 2\theta < 10^o$ range. For MCM$_C$ material the d_{100} value for reflection (100) was estimated to be 32.3 Å, corresponding to a lattice constant of $a = 37.3$ Å ($a = 2d_{100}/\sqrt{3}$), while in MCM$_{AW}$ the d_{100} value was 31.6 Å with a corresponding lattice constant of $a = 36.5$ Å. The XRD powder patterns and textural parameters described above were found to match the values reported in the literature for related systems [S5].

Table S2. Results of olefin epoxidation catalyzed by MCM-bpy-Mo catalyst at 353 K and after 24 h reaction time.

Olefin	Acetonitrile		Toluene	
	Conversion (%)	Yield (%)	Conversion (%)	Yield (%)
cis-Cyclooctene	78	78	92	92
Styrene	94	46[a]	100	25[a]
trans-Hex-2-en-1-ol	98	77[b]	99	85[b]
R-(+)-Limonene	34	34 (14 *Z*/18 *E*)[c]	98	98 (38 *Z*/60 *E*)[c]

[a] Benzaldehyde formed as major product; [b] *trans*-Hex-2-en-1-al formed as by-product; [c] Values in parenthesis refer to the yields of the *cis* (*Z*) and *trans* (*E*) epoxide diasteriomers.
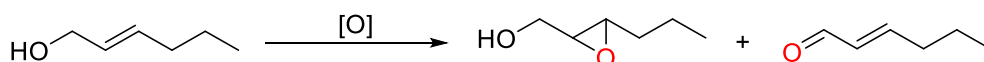
cis-Cyclooctene

4
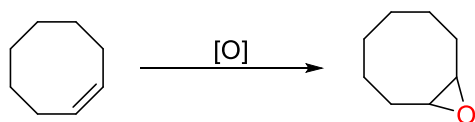
Styrene
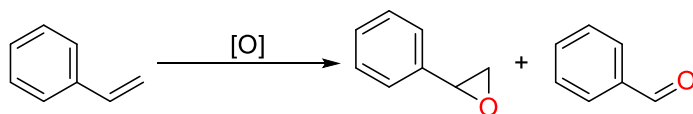
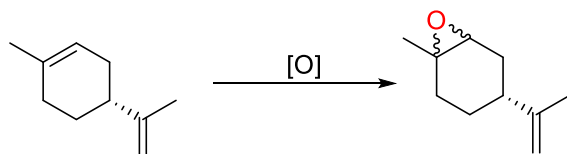*trans*-**Hex-2-en-1-ol**

R-(+)-**Limonene**

Figure S2. Oxidation products detected for the reactions shown in Table S1.

Computational details

DFT calculations [S6] were performed using the Gaussian09 program, revision D01 [S7], with the M06-2X hybrid functional, which includes a mixture of 54% Hartree–Fock exchange with DFT exchange correlation as developed by Thrular and Zhao [S8]. Pople's 6-311+G(d,p) basis set was used on all atoms [S9-S11]. All geometries were optimized without any geometry constraints at the level of theory mentioned above. The optimization approach also included the use of tight convergence criteria. To evaluate the effects of solvation, to account for the effects of solvent (acetonitrile and toluene) the IEFPCM model was used for the description of the solvent continuum. All geometries were found to be true minima as confirmed by calculation of vibrational harmonic frequencies, without any imaginary eigenvectors.

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G09 optimized geometries

Acetonitrile

```
-----------------------------------------------------------------------
---
#p m062x/6-311+g(d,p) scrf=(pcm,solvent=acetonitrile)
opt=(maxcyc=1000) scfcyc=1000 freq pop=(full,nboread)
-----------------------------------------------------------------------
---
```

```
Acetonitrile; E(RM062X) = -132.7412709
C        0.000000    0.000000   -1.176729
H        0.000000    1.026167   -1.542132
H        0.888686   -0.513083   -1.542132
H       -0.888686   -0.513083   -1.542132
C        0.000000    0.000000    0.280313
N        0.000000    0.000000    1.429270
```

```
Styrene oxide; E(RM062X) = -384.7916951
C        2.577169   -0.316014    0.075469
C        1.638189   -1.343783    0.012631
C        2.152951    1.009271    0.052940
H        1.964781   -2.377186    0.022016
H        2.877963    1.813576    0.095342
C        0.281867   -1.048475   -0.067024
C        0.795221    1.305795   -0.031039
H       -0.450376   -1.846272   -0.128388
H        0.465132    2.339197   -0.057018
C       -0.147281    0.279621   -0.084120
H        3.633942   -0.547494    0.136344
C       -1.598002    0.610532   -0.144130
H       -1.837496    1.616524   -0.477206
O       -2.464947   -0.395257   -0.655145
C       -2.573249   -0.070540    0.724672
H       -3.486360    0.440698    1.009597
H       -2.209201   -0.835420    1.404079
```

```
Styrene oxide – Acetonitrile Complex; E(RM062X) = -650.2872858
C        2.806948   -1.968615    0.366304
C        2.307763   -1.049972    1.288241
C        2.059172   -2.290466   -0.762939
H        2.884571   -0.799143    2.171087
H        2.439377   -3.007826   -1.480741
C        1.069712   -0.451839    1.079983
C        0.817700   -1.694302   -0.970480
H        0.677607    0.261172    1.797242
H        0.232397   -1.949694   -1.847852
C        0.319708   -0.766773   -0.054664
H        3.772345   -2.433111    0.529456
C       -0.991712   -0.109701   -0.307601
H       -1.645510   -0.612763   -1.015779
O       -1.666344    0.430300    0.823183
C       -1.165488    1.344313   -0.146122
```

```
H      -1.927378     1.850170    -0.730048
H      -0.312678     1.932913     0.179725
C       3.159177     1.302307    -1.095360
H       4.040616     0.809521    -0.685981
H       2.407779     0.547821    -1.334448
H       3.431998     1.849379    -1.997219
C       2.616854     2.226899    -0.109076
N       2.184973     2.958606     0.665523
C      -4.503668    -0.603601     0.930678
H      -5.507204    -1.021941     0.999103
H      -3.763731    -1.395843     1.039558
H      -4.351524     0.129844     1.720940
C      -4.327978     0.041689    -0.363399
N      -4.193123     0.543889    -1.388938
```

Toluene

#p m062x/6-311+g(d,p) scrf=(pcm,solvent=toluene) opt=(maxcyc=1000)
scfcyc=1000 freq pop=(full,nboread)

Toluene; E(RM062X) = -271.5066211
```
H      -0.012022     0.735762     2.139692
C       0.028664     2.416318     0.000000
H      -0.464283     2.822047     0.884771
H      -0.464283     2.822047    -0.884771
H       1.060241     2.779236     0.000000
C      -0.004244     0.910193     0.000000
C      -0.007531     0.194845    -1.198873
C      -0.007531    -1.196480    -1.201940
C      -0.006713    -1.897785     0.000000
C      -0.007531    -1.196480     1.201940
C      -0.007531     0.194845     1.198873
H      -0.012022     0.735762    -2.139692
H      -0.011746    -1.733231    -2.143489
H      -0.009644    -2.981132     0.000000
H      -0.011746    -1.733231     2.143489
```

Styrene oxide; E(RM062X) = -384.7881136
```
C       2.575520000    -0.309882000     0.090587000
C       1.641541000    -1.340575000     0.019089000
C       2.147152000     1.013379000     0.057396000
H       1.972123000    -2.372618000     0.033748000
H       2.868919000     1.820263000     0.105399000
C       0.285578000    -1.051048000    -0.079073000
C       0.790280000     1.304228000    -0.044367000
H      -0.445552000    -1.848443000    -0.153553000
H       0.456924000     2.336488000    -0.078442000
C      -0.147373000     0.274709000    -0.105123000
H       3.632263000    -0.537138000     0.165266000
```

9

```
C        -1.599076000      0.598085000     -0.180283000
H        -1.842262000      1.581786000     -0.573594000
O        -2.467166000     -0.435751000     -0.617402000
C        -2.566061000     -0.029189000      0.738219000
H        -3.479101000      0.495196000      1.000255000
H        -2.191354000     -0.747765000      1.461466000


Styrene oxide - Toluene Complex; E(RM062X) = -927.8234049
C        -1.944087      2.831816      0.173560
C        -0.742760      2.457605     -0.427701
C        -2.450382      2.080231      1.227573
H        -0.345999      3.037922     -1.253246
H        -3.389411      2.358772      1.692544
C        -0.055330      1.338384      0.023385
C        -1.762886      0.956153      1.676481
H         0.870604      1.030810     -0.451167
H        -2.173023      0.353494      2.480230
C        -0.562891      0.580595      1.080026
H        -2.483261      3.702030     -0.182998
C         0.152243     -0.633950      1.558383
H        -0.428126     -1.284132      2.208348
O         0.947540     -1.327524      0.603540
C         1.621093     -0.677904      1.671379
H         2.082305     -1.340724      2.397115
H         2.197873      0.197851      1.384481
C        -2.589159     -0.594346     -1.425594
C        -3.790273     -0.304386     -0.779265
C        -4.182544     -1.115567      0.288175
C        -3.396295     -2.187012      0.698897
C        -2.197645     -2.464253      0.046279
C        -1.796833     -1.663100     -1.017438
H        -2.259235      0.038290     -2.243618
H        -5.110128     -0.897302      0.808757
H        -3.716033     -2.802061      1.532923
H        -1.572266     -3.287779      0.371406
H        -0.848879     -1.854110     -1.507011
C        -4.648806      0.851877     -1.222199
H        -4.057105      1.591321     -1.764034
H        -5.451616      0.510135     -1.881918
H        -5.110669      1.346595     -0.365207
C         3.301654     -0.155909     -1.275422
C         3.633318      1.139343     -0.877519
C         4.533626      1.362593      0.163417
C         5.120259      0.286761      0.820099
C         4.803762     -1.012345      0.425498
C         3.904058     -1.228226     -0.610784
H         3.179480      1.985155     -1.385036
H         4.774900      2.377550      0.457898
H         5.821790      0.456400      1.628359
H         5.258306     -1.857756      0.929622
H         3.649152     -2.241968     -0.903018
C         2.291160     -0.408739     -2.363035
H         1.372093     -0.808031     -1.924388
H         2.046762      0.509516     -2.899816
H         2.664485     -1.139510     -3.083708
```