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Supporting information for article:

Rietveld Analysis of Computed Tomography and its Application to Methanol to Olefin Reactor Beds

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Supporting information

S1. **Refinement details/ fitting procedure** The Rietveld refinements presented were carried out using TOPAS academic version 4.2. Initial structural parameters from the SAPO-34 framework and carbon atoms placed on at positions where electron density peaks were observed in the cages in high resolution XRD studies were refined against the powder pattern of the central voxel of slice 0 for the relevant tomograph to obtain good starting values. A parametric Rietveld input file was then prepared using a simple text replacement script to copy the starting parameters into an input file which could be used to treat the powder patterns from the whole slice simultaneously. The command conserve_memory was added to the top of the input file before running to supress graphical output. Thus command should always be used when dealing with very large datasets such as these. An extract from a typical parametric input file is shown below. "…" indicates truncation of the input file. Complete input for one powder pattern is shown along with the essential initial "conserve_memory" command at the top of the file and continuation into the input for the next powder pattern at the end:

```
conserve_memory
…
'tomo_00_032_035
r_wp  27.439 r_exp  408.574 r_p  25.156 r_wp_dash  32.753 r_p_dash  47.883 r_exp_dash  487.701 weighted_Durbin_Watson  0.407 gof
0.067
'do_errors
iters 100000
xdd "TXT_MTO1_initial_sample_finaltomo_00_032_035.xy"
        start_X 0.6
        finish_X 8
        x_calculation_step 0.01
        bkg  @  0.136308454` -0.00497403061` -0.0316535491`  0.0179460652` -0.0265348765`  0.00656437511`  0.0291852131`
        lam
        ymin_on_ymax  0.8
        la  1 lo  0.142569 lh  0.002
User_Defined_Dependence_Convolution(gauss_fwhm, 5 Tan(2 Th),tth, 0.06948`)
        LP_Factor(0)
        Zero_Error(ze, 0.00110`)
prm oc1_00_032_035  0.39141`_LIMIT_MIN_0 max 3 min 0
prm oc2_00_032_035  1.01889`_LIMIT_MIN_0 max 3 min 0
prm oc3_00_032_035  0.89057`_LIMIT_MIN_0 max 3 min 0
prm totoc_00_032_035 =oc1_00_032_035+oc2_00_032_035+oc3_00_032_035;
local bp  1.37871`_LIMIT_MIN_0.01 max 10 min 0.01
local bo  0.19591`_LIMIT_MIN_0.01 max 10 min 0.01
        str
                Trigonal(atri_00_032_035  13.82297` , ctri_00_032_035  14.81201`)
                space_group "R-3"
```

```
                    site P1    x @  0.22554` y @  0.23150` z @  0.59983` occ P    0.92000    beq =bp; num_posns  18
                                                                  occ SI   0.08000    beq =bp; num_posns  18
                    site Al1   x @  0.01223` y @  0.22831` z @  0.61430` occ AL   1.00000    beq =bp; num_posns  18
                    site O1    x   0.99530      y   0.73270      z   0.48740      occ O    1.00000    beq =bo; num_posns  18
                    site O2    x   0.88010      y   0.75680      z   0.36900      occ O    1.00000    beq =bo; num_posns  18
                    site O3    x   0.80290      y   0.90560      z   0.38080      occ O    1.00000    beq =bo; num_posns  18
                    site O4    x   0.67520      y   0.98180      z   0.32920      occ O    1.00000    beq =bo; num_posns  18
                    site C1   x 0.93756 y 0.96891 z 0.96889 occ C =oc1_00_032_035;      beq 1.5 num_posns  18
                    site C2   x 0.92174 y 0.07793 z 0.84376 occ C =oc2_00_032_035;     beq 1.5 num_posns  18
                    site C3   x 0.00000 y 0.00000 z 0.06422 occ C =oc3_00_032_035;     beq 1.5 num_posns  6
                    scale sc  2.09022641e-011`
                    CS_L(size_00_032_035, 79.27213`_LIMIT_MIN_0.3)
Out_Yobs_Ycalc_and_Difference("MTO1_initial_sample_finaltomo_00_032_035.xyd")
Out_X_Yobs("MTO1_initial_sample_finaltomo_00_032_035.xy")
out "delme.txt" append
                                Out(Get (r_wp), "Rwp_00_032_035: %11.5f :")
                                Out(atri_00_032_035, " a_trigonal: %11.5f :", " %11.5f :")
                                Out(ctri_00_032_035, " c_trigonal: %11.5f :", " %11.5f :")
                                Out(bo, " Biso Oxygen: %11.5f :", " %11.5f :")
                                Out(bp, " Biso T sitep: %11.5f :", " %11.5f :")
                                Out(size_00_032_035, " xtal size L: %11.5f :", " %11.5f :")
                                Out(totoc_00_032_035, " occupancy of cage: %11.5f :", " %11.5f :
")
'al bond length restraints
Distance_Restrain(Al1 O3  2     1   0  -1, 1.73, 1.62277`, 0, 500)
Distance_Restrain(Al1 O2  5     -1  -1  -1, 1.73, 1.41855`, 0, 500)
Distance_Restrain(Al1 O1  5     -1  -1  -1, 1.73, 1.62063`, 0, 500)
Distance_Restrain(Al1 O4  2     1   0  -1, 1.73, 1.58233`, 0, 500)
'P bond length restraints
Distance_Restrain(P1 O1 3     -1   0   0, 1.53, 1.74449`, 0, 500)
Distance_Restrain(P1 O3 5     -1  -1  -1, 1.53, 1.75596`, 0, 500)
Distance_Restrain(P1 O4 12     0   1   0, 1.53, 1.71044`, 0, 500)
Distance_Restrain(P1 O2 5     -1  -1  -1, 1.53, 1.61488`, 0, 500)
'OPO angle restraints
Angle_Restrain(O1  3   -1   0   0 P1 O3   5   -1  -1  -1, 109.5, 106.84896`, 0, 0.01)
Angle_Restrain(O1  3   -1   0   0 P1 O2 5     -1  -1  -1, 109.5, 116.90964`, 0, 0.01)
Angle_Restrain(O1 3    -1   0   0 P1 O4 12     0   1   0, 109.5, 105.56820`, 0, 0.01)
Angle_Restrain(O2 5     -1  -1  -1 P1 O3 5     -1  -1  -1, 109.5, 109.61330`, 0, 0.01)
Angle_Restrain(O2 5     -1  -1  -1 P1 O4 12     0   1   0, 109.5, 111.63363`, 0, 0.01)
Angle_Restrain(O4 12     0   1   0 P1 O3 5     -1  -1  -1, 109.5, 105.56103`, 0, 0.01)
'oalo angle restraints
Angle_Restrain(O2 5     -1  -1  -1 Al1 O3 2     1   0  -1, 109.5, 118.24333`, 0, 0.01)
Angle_Restrain(O2 5     -1  -1  -1 Al1 O1 5     -1  -1  -1, 109.5, 110.55183`, 0, 0.01)
Angle_Restrain(O2 5     -1  -1  -1 Al1 O4 2     1   0  -1, 109.5, 115.27275`, 0, 0.01)
Angle_Restrain(O3 2     1   0  -1 Al1 O1 5     -1  -1  -1, 109.5, 102.85061`, 0, 0.01)
Angle_Restrain(O3 2     1   0  -1 Al1 O4 2     1   0  -1, 109.5, 107.35260`, 0, 0.01)
Angle_Restrain(O1 5     -1  -1  -1 Al1 O4 2     1   0  -1, 109.5, 100.42368`, 0, 0.01)
```

```
        xo_ls
                xo x_glass  2.33334059` I @  6.01803694e-006`_LIMIT_MIN_1e-010
               CS_L(, 9.90666)
'tomo_00_032_036
r_wp  18.855 r_exp  272.213 r_p  15.289 r_wp_dash  24.356 r_p_dash  30.379 r_exp_dash  351.622 weighted_Durbin_Watson  0.580 gof
0.069
'do_errors
iters 100000
xdd "TXT_MTO1_initial_sample_finaltomo_00_032_036.xy"
…
```

Table S1 lists the refined parameters and how they were treated (independent to each powder pattern or simultaneous refinement against all patterns in the parametric input file).

Table S1 Rietveld refinement parameters and refinement methods

Parameter	Number of parameters/powder pattern	How refined?		
		8 % Si Quench	8 % Si Fully Reacted	4 % Si Fully Reacted
Background	7	Individual Pattern	Individual Pattern	Individual Pattern
Tan theta Broadening	1	All Data	All Data	All Data
Zero error	1	All Data	All Data	All Data
Dummy carbon occupancy	3	Individual Pattern	Individual Pattern	Individual Pattern
Biso Phosphorus/aluminium	1	Individual Pattern*	Individual Pattern*	Fixed
Biso Oxygen	1	Individual Pattern*	Individual Pattern*	Fixed
x,y,z phosphorus	3	Individual Pattern	Individual Pattern	Individual Pattern
x,y,z aluminium	3	Individual Pattern	Individual Pattern	Individual Pattern
Scale	1	All Data	All Data	All Data
Lorentzian peak broadening	1	Individual Pattern	Individual Pattern	Individual Pattern
Glass peak position	1	All Data	All Data	All Data
Glass peak intensity	1	Individual Pattern	Individual Pattern	Individual Pattern
Glass peak broadening	1	All Data	Individual Pattern	Individual Pattern

* Refinement of the Biso parameters against all patterns in the tomographic slice was also tested. Maximum and minimum limits of 10 and 1 applied to Biso.

Figure S1 Location of the 5 tomographic slices on a sample reactor bed.

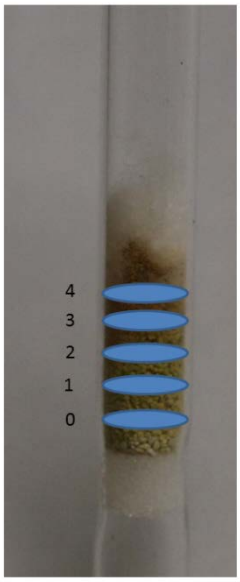


Figure S2 Average Rwp per tomographic slice for the 8% silicon SAPO-34 quenched after 5 minutes of MTO reaction. Error bars correspond to the standard deviation in the mean average.

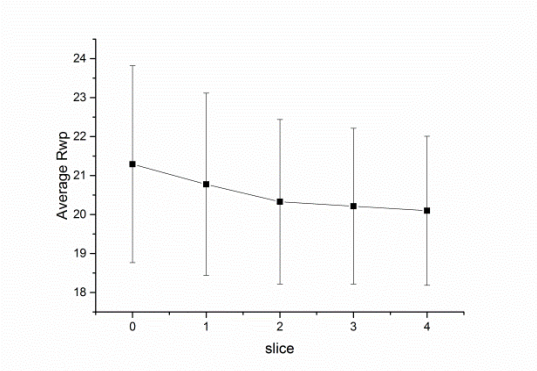
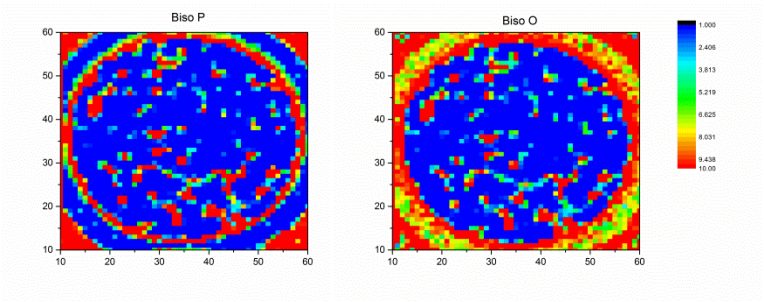


Figure S3 Tomographic slices 0 and 4 for quenched 8 % Si SAPO-34 reconstructed on Biso for the aluminium (left) and phosphorus/silicon (right) sites.

Slice 0



Slice 4

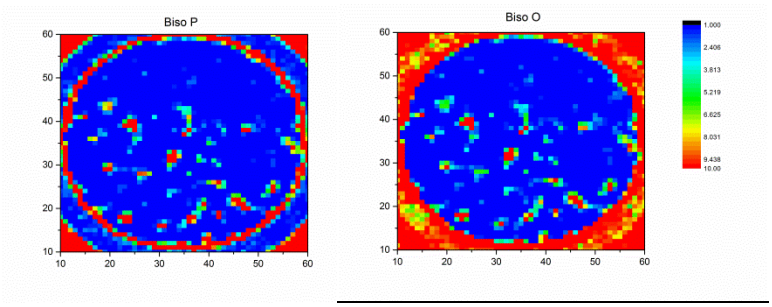


Figure S4 Reconstructions of the quenched 8 % Si SAPO-34 bed on x, y and z coordinates for aluminium (slices 0 and 4) and phosphorus (slice 4).

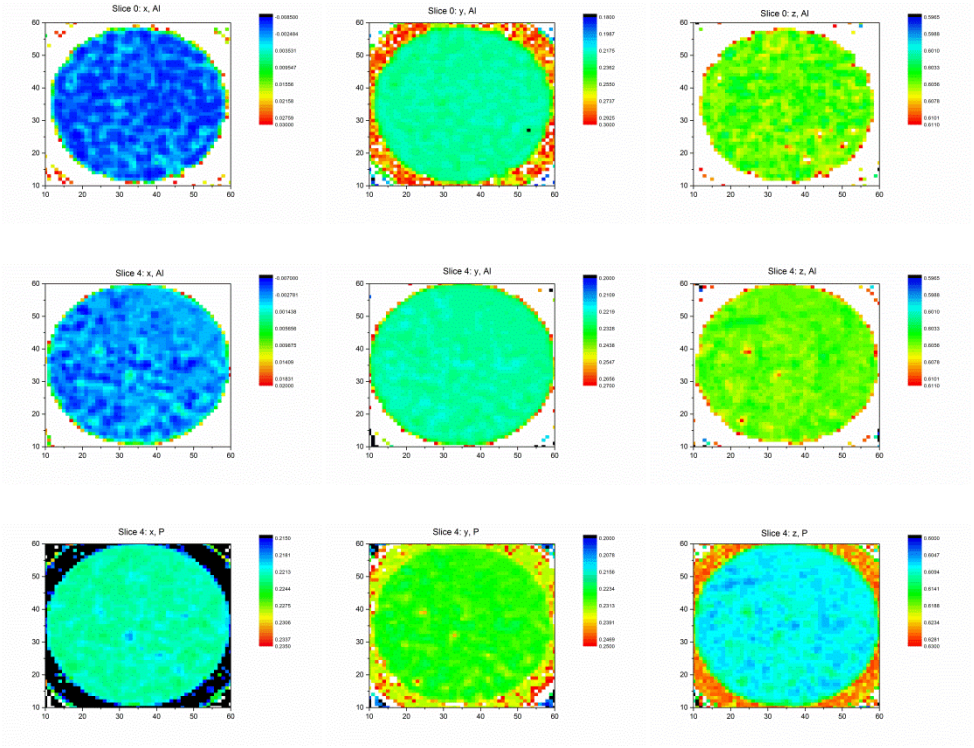


Figure S5 Reconstructions of the quenched 8 % Si SAPO-34 bed on peak broadening.

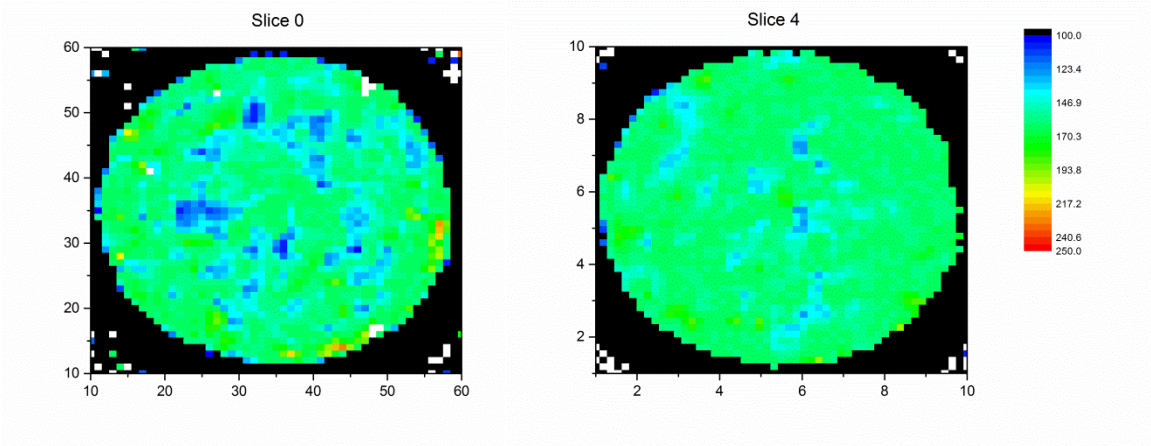


Figure S6 Tomographic slices for fully reacted 8 % Si SAPO-34 reconstructed on cage occupancy. (a) Slice closest to reactor inlet – (e) slice furthest from inlet.

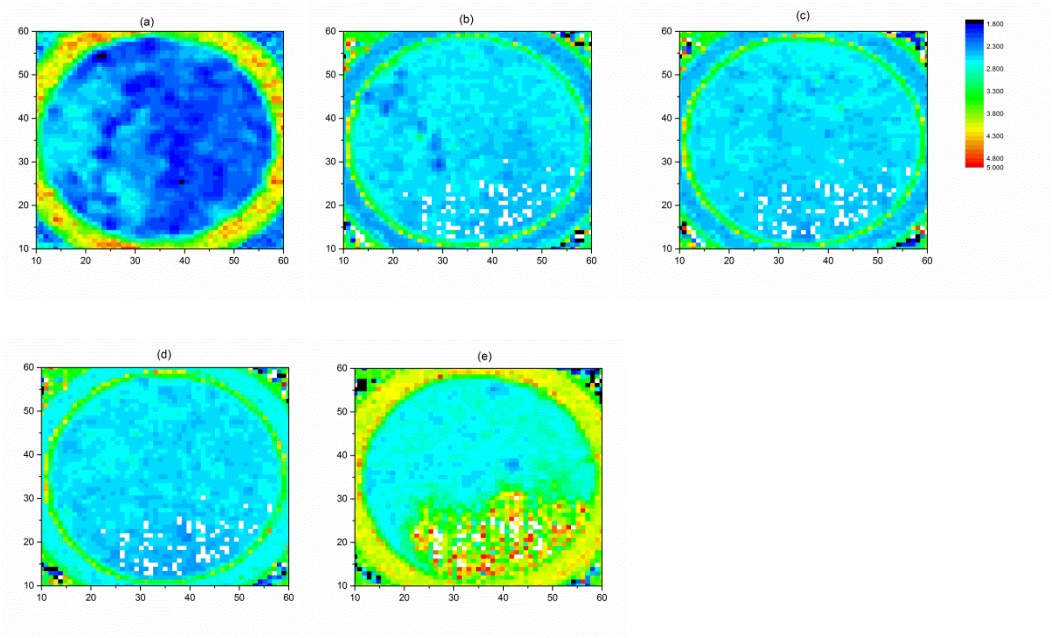


Figure S7 Comparison of the average *c*-axis variations in the tomographic slices compared to the z-scan data published previously (Wragg *et al.*, 2012)