Supporting information

Evolution of the polymorph selectivity of titania formation under acidic and low-temperature conditions

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1. Diffractograms
2. Polymorph selectivity
3. XRD Crystal morphology
4. Results of Rietveld refinements
1. Diffractograms
Diffractograms of samples from series B are shown in Figure S1 and series C in Figure S2.

**Figure S1.** X-ray diffractograms of samples B1-B4. The diffractograms are in the order of increasing reaction time, from bottom to top and offset in intensity for clarity.

**Figure S2.** X-ray diffractograms of samples C1-C4. The diffractograms are in the order of increasing reaction time, from bottom to top and offset in intensity for clarity.
Diffraction pattern of samples C1 and B4 with diamond internal standard added are shown in Figure S3. Sample C1 consists of mainly rutile polymorph but sample B4 is composed of mainly anatase and brookite polymorphs.

![Figure S3](image.png)

*Figure S3.* X-ray diffractograms of samples C1 and B4 mixed with diamond. The Bragg peak position for diamond is indicated with the letter D. The diffractograms are off-set in intensity for clarity.

2. Polymorph selectivity

Figure S4 shows the generation rate of the three titania phases in series A (i), series B (ii) and series C (iii). The generation rate is presented as mg formed of each phase in a single vial between sampling points divided by the time between sampling points, normalized to the initial mass of titania precursor (titanium (IV) n-butoxide) in the vial. Although the data is scattered, the graphs show that the selectivity for rutile formation is generally greater at high titania precursor concentrations and the selectivity for brookite and anatase is higher at intermediate and low precursor concentrations. It is, however, not straightforward to determine the generation rate from the data available from the synthesis. This is mainly due to the low number of possible sampling points, the uncertainty in quantifying the amorphous phase and the relatively small changes in phase composition between sampling points.
Figure S4. Generation rate of the three titania phases in series A (i), series B (ii) and series C (iii) presented as mg of each phase formed between two sampling points divided by the time between the sampling points and normalized to the initial mass of titania precursor in the vial. The instantaneous concentration of soluble titania precursor in the solution at the sampling points is calculated by subtracting the amount of titania precursor that has been converted to solid phases from the initial titania precursor used in each series. The instantaneous concentration of soluble titania precursor used in the graphs is the average between two subsequent sampling points.
3. XRD crystal morphology
The morphology of the formed crystals was obtained by advanced Rietveld analysis of the X-ray diffractograms. An example of the rutile morphology and the brookite morphology from samples A1 and A9, respectively, are shown in Figure S5.

Figure S5. Size and morphology of crystals obtained from XRD patterns and Rietveld analysis showing a prolate spheroid shaped rutile crystal (a) in sample A1 and an oblate spheroid shaped brookite crystal (b) obtained from sample A9. The axes units are nm.
4. Results of the Rietveld refinements
The refined unit cell parameters, isotropic crystal sizes, spherical harmonics coefficients and R
values obtained from the Rietveld refinements are listed in this section.

*Table S1.* Refined unit cell parameters for all samples.

| Sample | Rutile |  |  |  |  |  |  |  |  |  |  |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
|        | a=b    | a=b    | c      | a      | b      | c      | a=b    | a=b    | c      |
| A1     | 4.619  | 4.619  | 2.953  | 9.691  | 5.260  | 4.527  | 3.523  | 3.523  | 9.901  |
| A2     | 4.615  | 4.615  | 2.952  | 9.594  | 5.236  | 4.890  | 3.530  | 3.530  | 9.897  |
| A3     | 4.616  | 4.616  | 2.953  | 9.670  | 5.202  | 5.047  | 3.559  | 3.559  | 9.088  |
| A4     | 4.619  | 4.619  | 2.954  | 9.500  | 5.337  | 5.072  | 3.710  | 3.710  | 8.795  |
| A5     | 4.621  | 4.621  | 2.955  | 9.438  | 5.378  | 5.160  | 3.724  | 3.724  | 8.830  |
| A6     | 4.622  | 4.622  | 2.955  | 9.327  | 5.440  | 5.159  | 3.771  | 3.771  | 9.026  |
| A7     | 4.614  | 4.614  | 2.956  | 9.306  | 5.458  | 5.161  | 3.755  | 3.755  | 8.905  |
| A8     | 4.646  | 4.646  | 2.116  | 9.238  | 5.486  | 5.199  | 3.837  | 3.837  | 9.196  |
| A9     | 4.641  | 4.641  | 2.119  | 9.222  | 5.488  | 5.198  | 3.834  | 3.834  | 9.200  |
| B1     | 4.612  | 4.612  | 2.949  | 9.251  | 5.427  | 5.175  | 3.725  | 3.725  | 8.111  |
| B2     | 4.618  | 4.618  | 2.952  | 9.332  | 5.408  | 5.164  | 3.724  | 3.724  | 8.827  |
| B3     | 4.632  | 4.632  | 2.954  | 9.233  | 5.462  | 5.202  | 3.819  | 3.819  | 9.233  |
| B4     | 4.613  | 4.613  | 2.961  | 9.230  | 5.478  | 5.194  | 3.819  | 3.819  | 9.266  |
| C1     | 4.613  | 4.613  | 2.952  | 10.093 | 5.254  | 4.492  | 3.732  | 3.732  | 8.775  |
| C2     | 4.612  | 4.612  | 2.953  | 9.435  | 5.376  | 4.971  | 3.725  | 3.725  | 8.800  |
| C3     | 4.613  | 4.613  | 2.953  | 9.340  | 5.386  | 5.152  | 3.731  | 3.731  | 8.796  |
| C4     | 4.614  | 4.614  | 2.954  | 9.351  | 5.407  | 5.175  | 3.749  | 3.749  | 8.897  |
Table S2. Isotropic crystal size of the three phases in each sample.

| Sample | Isotropic size (Å) | Rutile | Anatase | Brookite |
|--------|--------------------|--------|--------|----------|
| A1     | 55.72              | *      | 20.87  |
| A2     | 57.45              | *      | 22.15  |
| A3     | 59.87              | *      | 22.84  |
| A4     | 62.09              | 56.18  | 23.82  |
| A5     | 62.09              | 37.72  | 26.99  |
| A6     | 64.44              | 41.19  | 31.87  |
| A7     | 72.41              | 35.13  | 31.99  |
| A8     | 41.1               | 24.75  | 48.65  |
| A9     | 43.24              | 24.32  | 50.77  |
| B1     | 61.47              | 43.32  | 28.67  |
| B2     | 63.51              | 40.43  | 29.67  |
| B3     | 61.44              | 26.03  | 36.99  |
| B4     | 68.46              | 24.75  | 38.98  |
| C1     | 59.25              | 28.80  | 26.40  |
| C2     | 61.81              | 39.07  | 27.34  |
| C3     | 61.84              | 33.36  | 27.35  |
| C4     | 68.00              | 36.47  | 33.44  |

*The relative weight fraction of anatase is very low in these samples and the size of the crystallites could therefore not be determined.
The shape of the crystals was described with spherical harmonics functions and the coefficients are shown in Table S3.

Table S3. The spherical harmonic coefficients for each phase in all samples analyzed. Maximum 4 coefficients were used to describe the shape.

| Sample | Rutile | Brookite | Anatase |
|--------|--------|----------|---------|
|        | Y00    | Y20      | Y40     | Y00    | Y20      | Y22+     | Y00    | Y20      | Y40     | Y44+     |
| A1     | 19.008 | -9.001   | -       | 51.440 | -       | -        | 2.902  | -       | -        | -        |
| A2     | 18.668 | -9.368   | -       | 60.115 | 51.813  | 20.064   | 3.547  | 1.034   | -        | -        |
| A3     | 17.646 | -8.863   | -       | 55.181 | 62.992  | 5.409    | 61.429 | 69.215  | -        | -        |
| A4     | 17.311 | -8.577   | -       | 49.689 | 54.199  | 3.490    | 28.149 | -10.10  | -        | -        |
| A5     | 17.048 | -8.500   | -0.451  | 44.839 | 47.250  | 4.454    | 28.140 | -6.766  | -        | -        |
| A6     | 16.512 | -8.726   | -0.622  | 34.227 | 22.710  | 9.237    | 30.532 | 13.461  | 0.878    | -        |
| A7     | 15.773 | -7.515   | -3.841  | 36.349 | 31.702  | 8.165    | 43.407 | 31.613  | -33.08   | -12.76   |
| A8     | 20.015 | -        | -       | 24.071 | -4.786  | 16.605   | 55.146 | 48.922  | -36.58   | 0.841    |
| A9     | 19.321 | -        | -       | 23.248 | -1.402  | 14.943   | 59.049 | 51.313  | -40.04   | 1.217    |
| B1     | 17.420 | -8.508   | -       | 39.267 | 30.948  | -        | 24.161 | -6.074  | -        | -        |
| B2     | 17.020 | -8.738   | -       | 40.384 | 39.128  | -        | 25.505 | -4.862  | -        | -        |
| B3     | 16.276 | -        | -       | 28.638 | 6.454   | 10.932   | 42.355 | 31.828  | -16.60   | -2.594   |
| B4     | 14.607 | -        | -       | 26.958 | 6.533   | 9.349    | 42.119 | 24.150  | -16.30   | -5.040   |
| C1     | 18.251 | -9.397   | -       | 71.482 | -51.60  | 87.152   | 53.939 | -42.90  | -        | -        |
| C2     | 17.485 | -8.982   | -       | 47.576 | 53.889  | -        | 33.608 | -22.56  | -        | -        |
| C3     | 17.442 | -8.867   | -       | 48.029 | 55.983  | -        | 42.472 | -31.27  | -        | -        |
| C4     | 16.258 | -9.182   | -       | 35.322 | 32.920  | -        | 27.122 | 4.455   | -        | -        |
Table S4. R-values for each phase in all samples.

| Sample | Rutile | Brookite | Anatase |
|--------|--------|----------|---------|
| A1     | 4.94   | 5.48     | 6.96    |
| A2     | 5.14   | 4.84     | 6.76    |
| A3     | 4.26   | 5.61     | 6.54    |
| A4     | 3.85   | 6.78     | 6.06    |
| A5     | 3.50   | 7.04     | 4.78    |
| A6     | 3.48   | 10.3     | 5.37    |
| A7     | 3.91   | 9.78     | 4.85    |
| A8     | 8.85   | 12.0     | 6.49    |
| A9     | 9.91   | 12.2     | 6.58    |
| B1     | 3.78   | 6.73     | 5.64    |
| B2     | 3.44   | 6.96     | 4.98    |
| B3     | 4.54   | 10.5     | 6.86    |
| B4     | 4.84   | 10.9     | 7.48    |
| C1     | 2.50   | 4.81     | 5.22    |
| C2     | 3.78   | 6.38     | 5.76    |
| C3     | 3.78   | 6.06     | 5.84    |
| C4     | 3.47   | 8.30     | 5.06    |