In-Situ High-Resolution Powder X-Ray Diffraction Study of UiO-66 Under Synthesis Conditions in a Continuous-Flow Microwave Reactor

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ELECTRONIC SUPPLEMENTARY INFORMATION



Figure S1. Experimental setup for the synthesis of UiO-66 employed during this work. Schematic representation (a); picture of the actual setup positioned at the beamline for *in-situ* HR-PXRD measurements (b); close-up picture of the outlet tube placed in the focus of the X-ray beam (c).

Residence time (min)	Zr-stock flow rate (mL/min)	bdc-stock flow rate (mL/min)	Stock process time (min)	Stock process volume (mL)	Unloading flow rate (mL/min)	Unloading time (min)	Unloading volume (mL)	Flushing flow rate (mL/min)	Flushing time (min)	Flushing volume (mL)	Total experiment time (min)	Total experiment volume (mL)
1	4.16	2.08	4.00	24.96	6.24	1.28	8	8	2	16	7.28	48.96
3	1.39	0.69	4.00	8.32	2.08	3.85	8	8	2	16	9.85	26.17
5	0.83	0.42	6.41	8	1.25	6.41	8	8	2	16	14.82	32
7	0.59	0.30	8.97	8	0.89	8.97	8	8	2	16	19.95	32
9	0.46	0.23	11.54	8	0.69	11.54	8	8	2	16	25.08	32
11	0.38	0.19	14.10	8	0.57	14.10	8	8	2	16	30.21	32
13	0.32	0.16	16.67	8	0.48	16.67	8	8	2	16	35.33	32

Table S1. Detailed processing parameters for a series of experiments in the range of residence time between 1 and 13 minutes. A minimum stock process time (4 minutes) and volume (8 mL) were set in order to ensure sufficient statistics.

Data treatment.

The 3.5 to $6.2^{\circ} 2\theta$ -range was used for gathering information, because no diffraction from the PTFE tube was present in this region (Figures S2-3). The intensity and full width at half maximum (FWHM) of the (111), (200) and (220) reflections, positioned at 3.69, 4.27 and 5.96° 2 θ , respectively, were extracted by single-peak refinement employing the program TOPAS 5.0. The same two parameters for FWHM (Gaussian and Lorentzian) were refined for each peak, setting a maximum limit (0.05 or 0.1, depending on the experiment) to prevent the program from forcing unrealistic refinement of very broad peaks to fit patterns where no diffraction from the MOF was detected. For the same purpose, limits were also set for the position of the reflections. A third-order Chebyschev polynomial function was used to model the background. The wavelength value of 0.77625 Å was obtained by refining the pattern of a Si640d standard measured prior to *in-situ* experiments.

The data obtained from the refinements was mathematically treated to extract the information: intensities with calculated errors higher than 10% were set as zero, based on the fact that they corresponded to patterns where no MOF peaks existed, while the two components of FWHM were summed up. Since the evolution of the intensity and full width at half maximum (FWHM) of different reflections was the same (Figure S4), we chose the (111) reflection, which is the most intense one, to extract information. The mean values for intensity and FWHM of the (111) reflection (hereafter I_{111} and FWHM₁₁₁, respectively) were obtained with the following procedure:

- all the points of the stock process and unloading phases having $I_{111} = 0$ were discarded;
- the FWHM₁₁₁ values for the remaining points were plotted and fitted with an ExpDec1 function [y = A1*exp(-x/t1) + y0] in the program Origin 2015;
- the first derivative of the fitting curve was calculated and a limit of -0.005 for its value was arbitrarily set to separate the preliminary stage and the steady state one (Figure S5);
- the average FWHM₁₁₁ was calculated from the points falling in the steady state region;
- the value for I_{111} was obtained by averaging over the points having intensity > 80% of the highest observed I_{111} in the steady state region, assuming that lower values were due to the presence of bubbles, which attributed to boiling of the reaction mixture and caused intermittent flow and exposition of variable amounts of reaction solution to the X-ray beam.

Standard deviations were calculated for $FWHM_{111}$ with respect to the average value calculated over the steady state region. The heavy mathematical treatment necessary to extract information about the intensities prevented us from estimating reliable errors on I_{111} . An overall description of each series of experiments was obtained by plotting the average values of I_{111} and $FWHM_{111}$ at the steady state as functions of residence time: the former accounts for the amount of diffracting matter interacting with the X-ray beam and is here used to estimate the yield of the reaction, whereas the latter can be used as a measure of crystallite size (as a rule of thumb, the larger $FWHM_{111}$ the smaller the crystallite size).



Figure S2. Representative PXRD pattern of the 1 mm ID PTFE tube filled with slurry containing UiO-66.



Figure S3. Enlargement of the -6 to 6° region of the pattern in Figure S4 showing the reflections of UiO-66.



Figure S4. Comparison between the intensities of the (111) reflection (black symbols) and of the (200) reflection (red symbols) for experiment **36w30a_07**, showing that they have the same trend.



Figure S5. Fit of the FWHM₁₁₁ evolution in the 7-16 mL range with an exponential decay function for experiment **36w30a_07**. The gray line marks the separation between the preliminary stage and the steady state, when the first derivative of the fitting curve is >-0.005.



Figure S6. Plots of I_{111} and FWHM₁₁₁ as functions of volume of reaction solution processed for series **12w15a**.



Figure S7. Plots of I₁₁₁ and FWHM₁₁₁ as functions of volume of reaction solution processed for series **12w30a**.



Figure S8. Plots of I_{111} and FWHM₁₁₁ as functions of volume of reaction solution processed for series **24w15a**.



Figure S9. Plots of I_{111} and FWHM₁₁₁ as functions of volume of reaction solution processed for series **24w30a**.



Figure S10. Plots of I₁₁₁ and FWHM₁₁₁ as functions of volume of reaction solution processed for series **24w30a***.



Figure S11. Plots of I_{111} and FWHM₁₁₁ as functions of volume of reaction solution processed for series **24w60a**.



Figure S12. Plots of I_{111} and FWHM₁₁₁ as functions of volume of reaction solution processed for series **36w15a**.



Figure S13. Plots of I_{111} and FWHM₁₁₁ as functions of volume of reaction solution processed for series **36w30a**.



Figure S14. Plots of I₁₁₁ and FWHM₁₁₁ as functions of volume of reaction solution processed for series **36w60a**.



Figure S15. Plot of I_{111} (squares) and FWHM₁₁₁ (circles) as functions of residence time for experiments **12w30a** (blue), **24w30a** (purple) and **36w30a** (gray), carried out varying the amount of water (12, 24, 36 moles, respectively) in the presence of a fixed amount of acetic acid (30 moles).



Figure S16. Plot of I₁₁₁ (squares) and FWHM₁₁₁ (circles) as functions of residence time for experiments **24w60a** (orange) and **36w60a** (green), carried out varying the amount of water (24, 36 moles, respectively) in the presence of a fixed amount of acetic acid (60 moles).



Figure S17. Plot of I₁₁₁ (squares) and FWHM₁₁₁ (circles) as functions of residence time for experiments **12w15a** (black) and **12w30a** (blue), carried out varying the amount of acetic acid (15, 30 moles, respectively) in the presence of a fixed amount of water (12 moles).



Figure S18. Plot of I₁₁₁ (squares) and FWHM₁₁₁ (circles) as functions of residence time for experiments **24w15a** (dark green), **24w30a** (purple) and **24w60a** (orange), carried out varying the amount of acetic acid (15, 30, 60 moles, respectively) in the presence of a fixed amount of water (24 moles).



Figure S19. Plot of I₁₁₁ (squares) and FWHM₁₁₁ (circles) as functions of residence time for experiments **24w15a** (dark green), **36w30a** (gray) and **24w30a*** (red).



Figure S20. PXRD patterns of 36w15a_05 (black line) and 36w15a_09 (red line).



Figure S21. PXRD patterns of 24w30a*_07 (black line) and 24w30a*_13 (red line).



Figure S22. PXRD patterns of 36w30a_05 (black line) and 36w30a_09 (red line).



Figure S23. PXRD patterns of 36w60a_05 (black line) and 36w60a_09 (red line).



Figure S24. TEM micrograph of 36w15a_05.



Figure S25. TEM micrograph of 24w30a*_07



Figure S26. TEM micrograph of 36w30a_09



Figure S27. TEM micrograph of 36w60a_05



Figure S28. Thermogravimetric curves of 36w15a_05 (black line) and 36w15a_09 (red line).



Figure S29. Thermogravimetric curves of 24w30a*_07 (black line) and 24w30a*_13 (red line).



Figure S30. Thermogravimetric curves of 36w30a_05 (black line) and 36w30a_09 (red line).



Figure S31. Thermogravimetric curves of 36w60a_05 (black line) and 36w60a_09 (red line).



Figure S32. Nitrogen sorption isotherms of **36w15a_05** (black circles) and **36w15a_09** (red circles).



Figure S33. Nitrogen sorption isotherms of **24w30a*_07** (black circles) and **24w30a*_13** (red circles).



Figure S34. Nitrogen sorption isotherms of **36w30a_05** (black circles) and **36w30a_09** (red circles).



Figure S35. Nitrogen sorption isotherms of **36w60a_05** (black circles) and **36w60a_09** (red circles).