Supplementary Material

In order to better examine the signal from the W-containing crystallites in the W/A150 samples, reference background samples were prepared using physical mixtures of silica (A150) and crystalline WO_3. These reference samples (WO_3 + A150) contained WO_3 amounts calculated to give W loadings equal to the W/A150 samples. The diffraction pattern of each reference sample was taken immediately after its corresponding W/A150 sample to reduce errors resulting from X-ray intensity changes over time. The sharp peaks from the large WO_3 crystallites in the reference samples allowed the separation of the support signal (true background plus Aerosil 150 signal) from the monoclinic WO_3 signal via Rietveld refinement (Figure S-1.). TOPAS V6 was used to refine the support signal (true background plus amorphous silica signal) from the reference diffractograms (WO_3+A150) using two crystal structures based on the structure provided in (PDF 04-005-4272), but with separate refinements of the lattice parameters, particle size, atomic coordinates, and thermal parameters.

Once isolated, the support signal from each reference sample was substituted in as the background for the analysis (also using TOPAS V6) of its corresponding W/A150 diffractogram. The whole-pattern fits to the W/A150 samples used only two refine-able parameters for each structure: the overall structure scaling factor and the particle size (derived from Gaussian peaks). Lattice parameters and any thermal parameters were fixed at the values reported in literature (see Table 1 for the structure references). Lorentz-Polarization, absorbance, and overspill (a.k.a. beam spill) scaling factors were all scaled point-by-point. The beam spill macro was further modified for increased accuracy. Figure S2. shows the W/A150 diffractograms with their corresponding support signals subtracted.

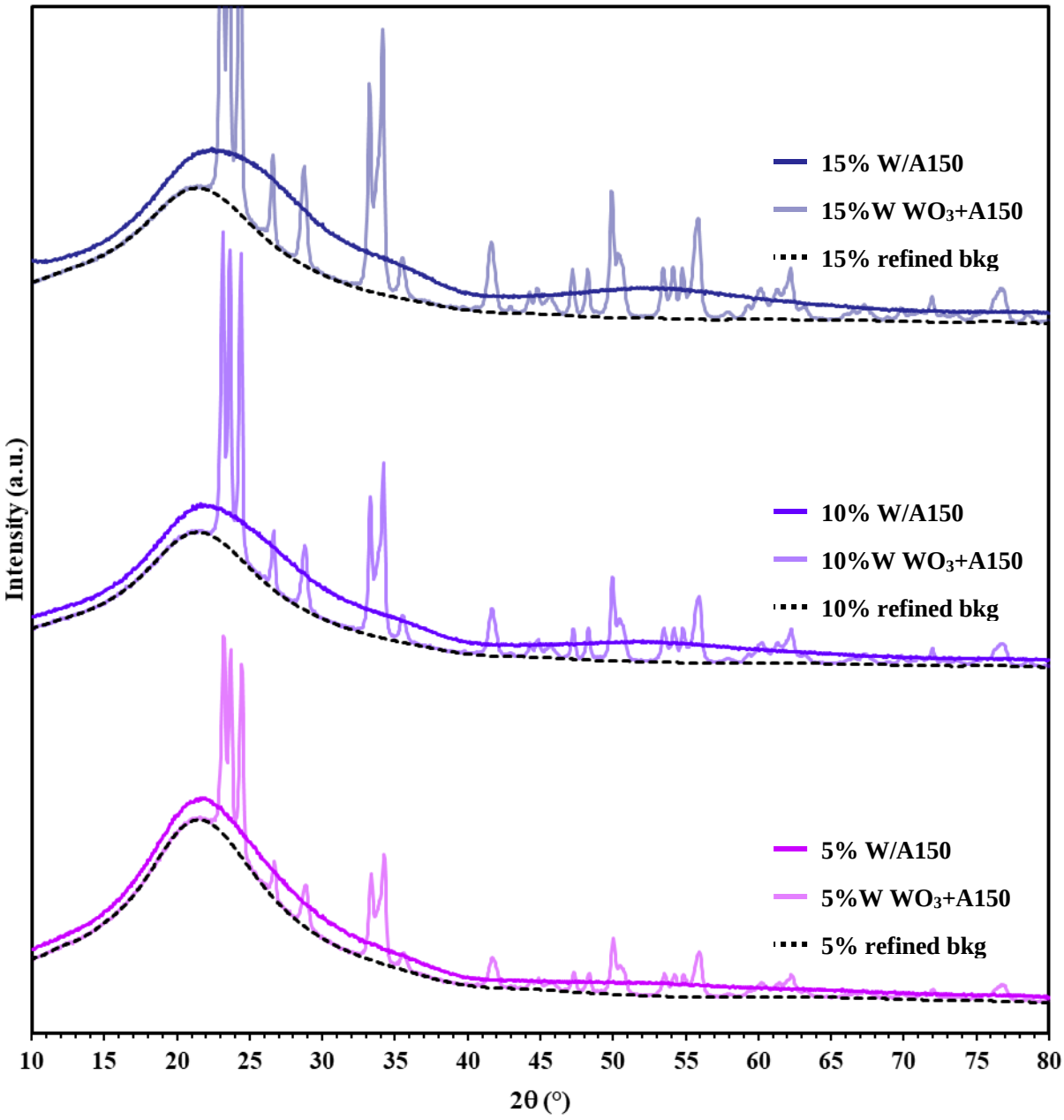

Figure S1. 15%, 10%, and 5% W/A150 XRD patterns showing for each sample the raw XRD pattern (W/A150), the raw reference pattern (WO_3+A150) showing sharp peaks, and the background (sample holder plus A150 support) which was refined from the reference pattern and then used as the background for the analysis of the W/A150 samples.

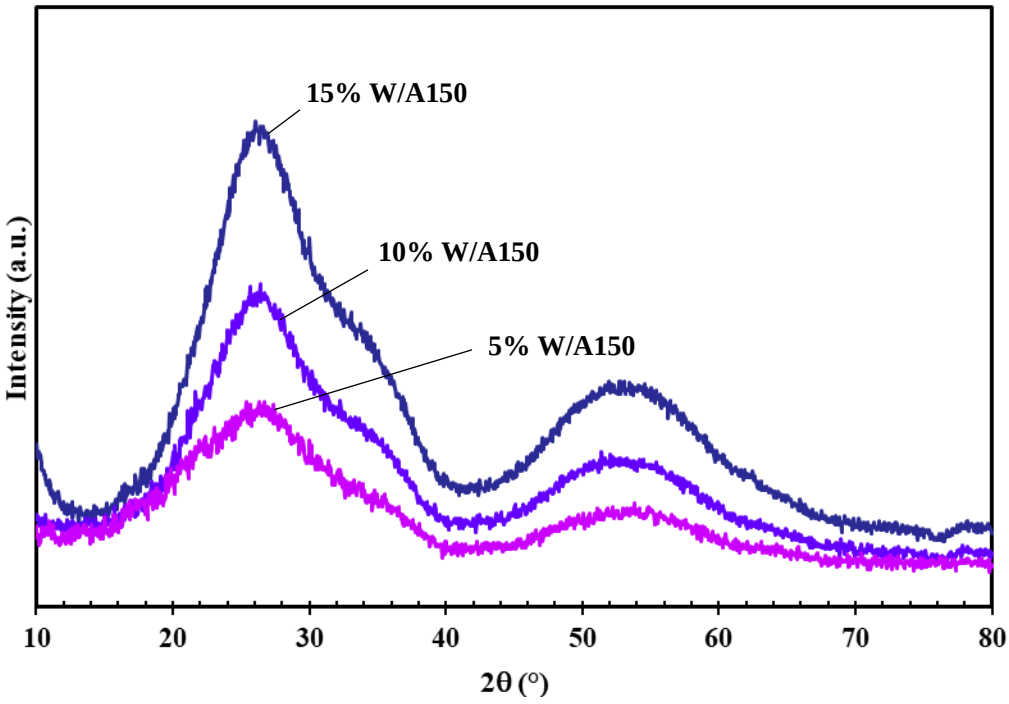

Figure S2. W/A150 diffraction patterns after subtracting the background and silica support signals.

In Figure S2, the displayed remaining portions of the original diffractograms represent the isolated XRD signal from the WO_3 crystallites. All three samples show the same general shape, suggesting that the same crystalline phase is present in each sample. The patterns show no isolated peaks with which to estimate particle size, therefore further analysis requires a whole-pattern fit (see Figures S3 to S5).

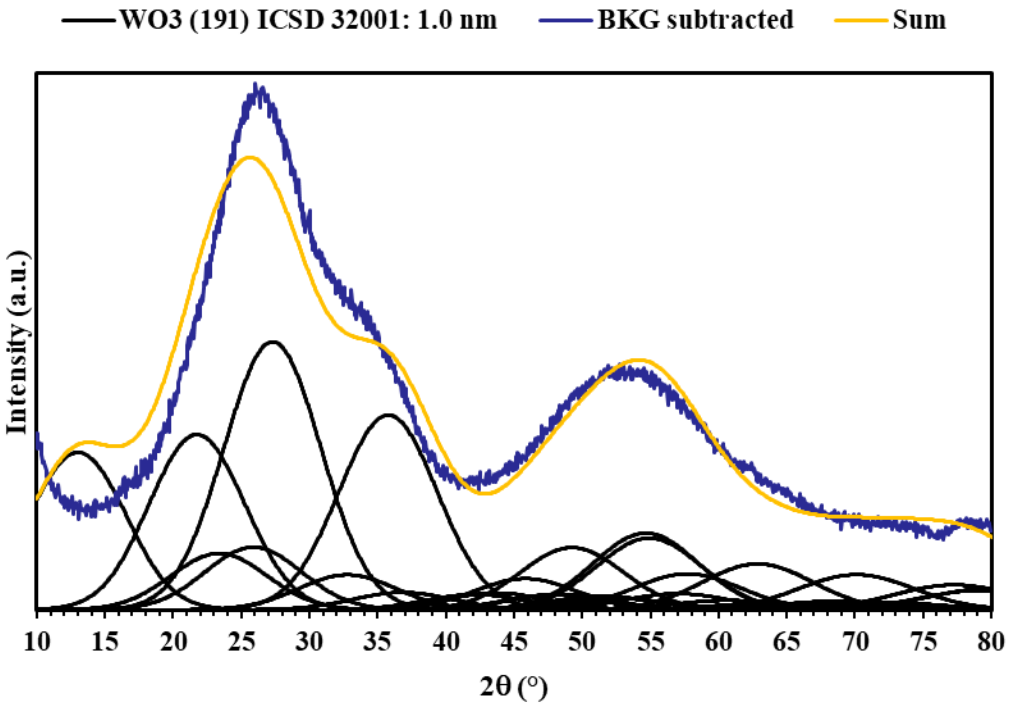

Figure S3. 15% W/A150: fit to hexagonal WO_3 (ICSD 32001)

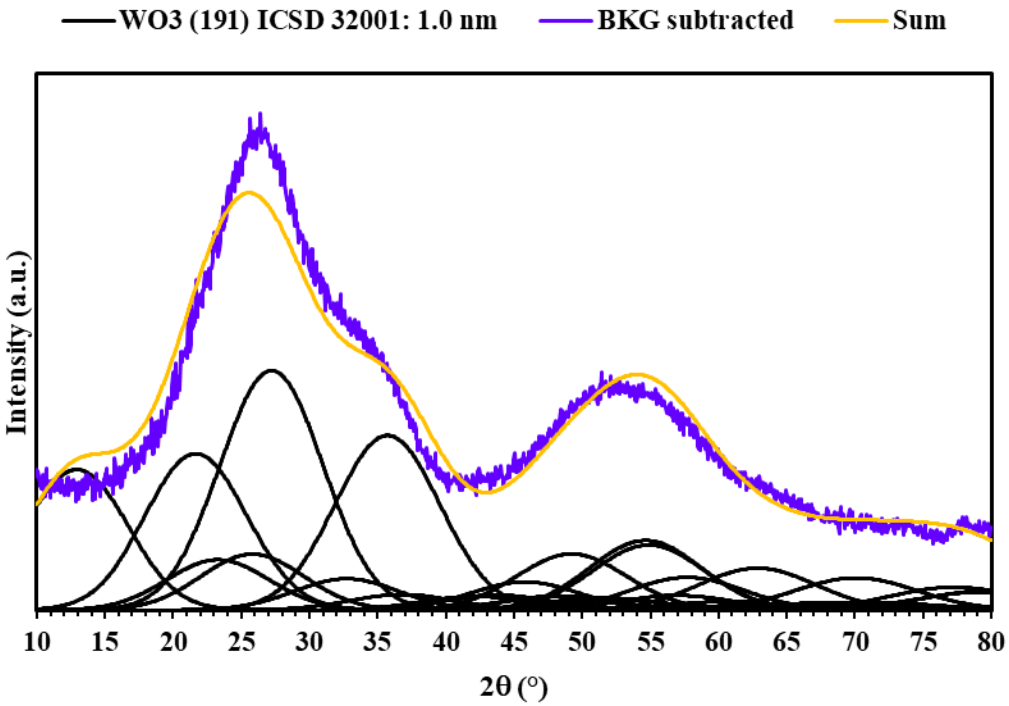

Figure S4. 10% W/A150: fit to hexagonal WO_3 (ICSD 32001)

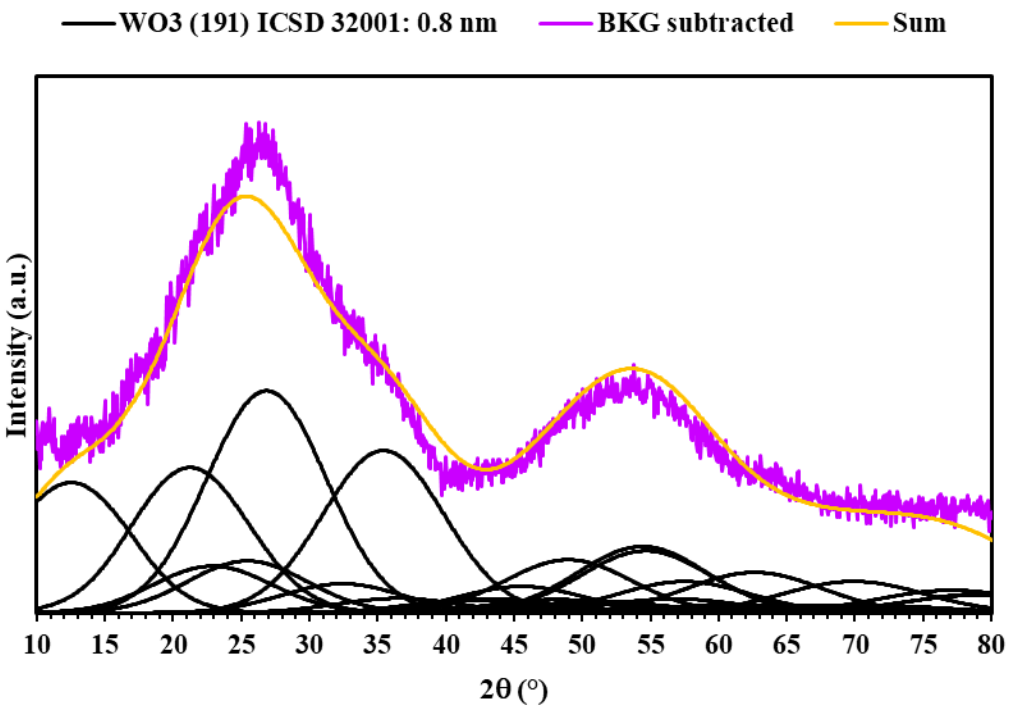

Figure S5. 5% W/A150: fit to hexagonal WO_3 (ICSD 32001)

Table S1 lists the structures used to fit the W/A150 patterns. For each of the W/A150 samples the best fit belonged to a hexagonal phase of WO_3 [52] with particle sizes on the order of 1 nm. There appears to be a slight increasing trend in particle size with weight loading. As weight loading increases, the closeness of the fit decreases – possible reasons for this include imperfect background isolation and the presence of unknown crystalline phases. Due to the discrepancies in the fits, especially in the higher tungsten weight loadings, it is only assumed that the crystallite sizes are less than 2 nm in size. It is noted that the individual WO_3 peak positions appear shifted in the figure from the bulk positions; this is a real effect resulting from scaling factors (mainly Lorentz-Polarization) applied point-by-point to broad peaks.

For the W-KIT-5 samples such an analysis was not possible because the W is incorporated into the structure of the silica [47]; the structure of the silica support without W is different and gives a shifted amorphous peak position in comparison to the samples containing W. Because of this there is no way to obtain a completely independent silica signal in a reference sample with large crystallites. Our attempts to make a reference sample using pure KIT-5 resulted in inaccurate isolated crystal signals that could not be reasonably fit by any of the structures in Table

1. The most that can be said from our attempts is that the crystallite sizes for the W-KIT-5 samples appear to be similar to those of the W/A150 samples.

Table S1. Crystal Structures used to fit the isolated crystallite XRD signals for the WO_3/A150 samples. Quality of fit (R_{wp}) values are given for each individual structure's best fit to each of the W/A150 samples (smaller R_{wp} = better fit).

Structure Information				**15% WO_3/A150**		**10% WO_3/A150**		**5% WO_3/A150**	
Crystal Family	Space Group	Chemical Formula	Reference	R_{wp}	Size (nm)	R_{wp}	Size (nm)	R_{wp}	Size (nm)
Triclinic	2	WO_3	ICSD 1620	7.17	0.8	4.96	0.8	2.8	0.6
Monoclinic	7	WO_3	ICSD 84168	6.97	0.8	4.82	0.8	2.8	0.6
	10	$W_{18}O_{49}$	ICSD 202488	6.06	0.9	4.30	0.8	2.7	0.7
	13	$W_{25}O_{73}$	ICSD 392	7.42	0.8	4.92	0.8	2.6	0.7
	14	WO_3	PDF04-005-4272	7.13	0.8	4.91	0.8	2.8	0.7
	14	WO_3	ICSD 31823	7.37	0.8	4.96	0.7	2.6	0.6
	14	WO_3	ICSD 80057	7.32	0.9	5.06	0.8	3.0	0.7
	14	WO_3	ICSD 84848	6.88	0.8	4.83	0.8	2.8	0.6
Ortho-rhombic	21	WO_3	ICSD 73719	6.23	0.7	4.76	0.6	3.2	0.5
	35	$WO_{1.09}$	ICSD 71912	11.6	0.3	8.35	0.3	4.7	0.3
	55	W_3O_8	ICSD 73720	6.12	0.9	4.50	0.7	2.8	0.6
	55	$WO_{2.6}$	ICSD 72544	6.24	0.9	4.68	0.8	2.9	0.6
	60	WO_3	ICSD 50728	7.54	0.8	5.17	0.8	2.9	0.6
	62	WO_2	ICSD 74774	9.97	0.7	7.20	0.6	4.4	0.6
	62	WO_3	ICSD 836	7.92	0.8	5.40	0.8	3.0	0.7
Tetragonal	113	WO_3	ICSD 86144	7.36	0.8	5.03	0.8	2.8	0.6
	129	WO_3	ICSD 27962	10.2	0.8	7.16	0.8	4.0	0.7
	129	WO_3	ICSD 88367	8.14	0.8	5.52	0.7	3.0	0.7
	129	WO_3	ICSD 89092	8.90	0.8	6.01	0.7	3.1	0.7
	130	WO_3	ICSD 50733	7.91	0.8	5.37	0.8	2.9	0.7
	136	WO_2	ICSD 647647	7.98	0.6	5.88	0.6	3.6	0.5
Hexagonal	191	WO_3	ICSD 32001	4.27	1.0	2.63	1.0	1.5	0.8
	193	WO_3	ICSD 80635	4.37	1.0	2.81	0.9	1.8	0.8
Cubic	221	WO_3	ICSD 108651	8.67	0.7	5.76	0.7	2.8	0.6
	224	Keggin	PDF04-011-8671	17.7	0.9	13.0	0.8	7.0	0.8
	224	Keggin	ICSD 95623	6.54	1.2	4.68	1	2.6	0.9
	229	W	ICSD 43421	11.4	0.3	8.23	0.3	4.7	0.3