Chemistry of Materials

Morphological and Kinetic Studies on Hexagonal Tungstates

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Table S1. Synthesis of HTB-/P alkali tungstates(VI) with soft chemistry methods

Compound	Type	Synthesis	Precursor	Lit.
$(1.03-1.32)\text{Li}_2\text{O}\cdot\text{WO}_3\cdot(0.74-0.99)\text{H}_2\text{O}$	O	solution	M_2WO_4 , HCl or HNO_3 , 100 °C	[1]
$\text{Li}_{0.20}\text{WO}_{3.10}\cdot 0.5\text{H}_2\text{O}$	HTB	hydrothermal	M_2WO_4 , HCl, 155 °C	[2]
$\text{Li}_{(0.10-0.42)}\text{WO}_{(3.05-3.21)}\cdot 0.56-0.88\text{H}_2\text{O}$	HTB	solution	Li_2WO_4 , HCl, 125 - 200 °C	[3]
$(0.08-0.14)\text{Na}_2\text{O}\cdot\text{WO}_3\cdot(0.67-0.85)\text{H}_2\text{O}$	HTB	solution	M_2WO_4 , HCl or HNO_3 , 100 °C	[1]
$\text{Na}_{0.26}\text{WO}_{3.13}\cdot 0.5\text{H}_2\text{O}$	HTB	hydrothermal	M_2WO_4 , HCl, 155 °C	[2]
$\text{Na}_{0.55}\text{WO}_{3.275}$	P	hydrothermal	M_2WO_4 , HCl, 155 °C	[2]
$0.33\text{K}\text{O}_{0.5}\cdot\text{WO}_3$	HTB	solution	M-IPA and MCl, RT	[4]
$(0.07-0.11)\text{K}_2\text{O}\cdot\text{WO}_3\cdot(0.49-0.67)\text{H}_2\text{O}$	HTB	solution	M_2WO_4 , HCl or HNO_3 , 100 °C	[1]
$\text{K}_x\text{W}_{1-y/6}\text{O}_3$	HTB	heating	K-IPA, air, 500 °C	[5]
$0.23\text{Rb}\text{O}_{0.5}\cdot\text{WO}_3$	HTB	solution	M-IPA and MCl, RT	[4]
$\text{Rb}_x\text{WO}_{3+x/2}$	P	hydrothermal	M_2WO_4 , HCl, 155 °C	[2]
$\text{Rb}_{1.1}\text{W}_{1.65}\text{O}_{5.5}$	P	solid state	h- WO_3 , Rb_2CO_3 , 300 °C	[6]
$\text{Cs}_x\text{W}_{1-y/6}\text{O}_3$ (x = 0.3)	HTB	solution	Cs-poor IPA and CsCl, RT	[7]
$\text{Cs}_x\text{W}_{1-y/6}\text{O}_3$	P	solution	Cs-rich IPA and CsCl	[7]
$0.45\text{Cs}\text{O}_{0.5}\cdot\text{WO}_3$	P	solution	M-IPA and MCl, RT	[4]
$(\text{Cs}_2\text{O})_x\text{W}_2\text{O}_6$ (0.3 < x < 0.5)	P	solution	$\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$, HCl, Cs_2CO_3 , 90 °C	[8]
$\text{Cs}_x\text{WO}_{3+x/2}$	P	hydrothermal	M_2WO_4 , HCl, 155 °C	[2]
$\text{Cs}_x\text{WO}_{3+y}$	P	ball-milling	WO_3 , Cs_2CO_3	[1]
$\text{Cs}_{1.1}\text{W}_{1.65}\text{O}_{5.5}$	P	solid state	h- WO_3 , Cs_2CO_3 , 300 °C	[6]
$(0.04-0.073)\{(\text{NH}_4)_2\text{O}\}\cdot\text{WO}_3\cdot(0.38-0.82)\text{H}_2\text{O}$	HTB	solution	M_2WO_4 , HCl or HNO_3 , 100 °C	[1]
$(\text{NH}_4)_{0.20}\text{WO}_{3.10}$	HTB	hydrothermal	M_2WO_4 , HCl, 155 °C	[2]
$\text{Ba}_x\text{W}_{1-y/3}\text{O}_3$	2D-P	solution	M-IPA and MCl_2 , RT	[4]
$\text{Tl}_x\text{W}_{1-y/6}\text{O}_3$	2D-P	solution	M-IPA and MCl_2 , RT	[4]
$\text{Pb}_x\text{W}_{1-y/3}\text{O}_3$	2D-P	solution	M-IPA and MCl_2 , RT	[4]

Literature: Table S1

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Table S2. The rate equations for solid state reactions reported in literature^[1-3]

Growth Model		Rate Equation $f(\alpha) = kt$	m
Diffusion controlled			
$D_1(\alpha)$		$\alpha^2 = 0.25 (t/t_{0.5})$	0.62
$D_2(\alpha)$		$(1-\alpha) \ln (1-\alpha) + \alpha = 0.1534 (t/t_{0.5})$	0.57
$D_3(\alpha)$	[Jander]	$[1-(1-\alpha)^{1/3}]^2 = 0.0425 (t/t_{0.5})$	0.54
$D_4(\alpha)$	[Ginstling-Brounshtein]	$1-2\alpha/3-(1-\alpha)^{2/3} = 0.0367 (t/t_{0.5})$	0.57
Phase-boundary controlled			
$R_2(\alpha)$		$1-(1-\alpha)^{1/2} = 0.2929 (t/t_{0.5})$	1.11
$R_3(\alpha)$		$1-(1-\alpha)^{1/3} = 0.2063 (t/t_{0.5})$	1.07
First order			
$F1(\alpha)$		$[-\ln(1-\alpha)] = 0.6931 (t/t_{0.5})$	1.00
Nucleation [Avrami-Erovéef]			
$A2(\alpha)$		$[-\ln(1-\alpha)]^{1/2} = 0.8326 (t/t_{0.5})$	2.00
$A3(\alpha)$		$[-\ln(1-\alpha)]^{1/3} = 0.885 (t/t_{0.5})$	3.00

References

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Figure S1. Representative SEM images of lithium tungstates synthesized under standard conditions.

Figure S2. Representative SEM images of Na-HTB tungstate rods synthesized under standard conditions (a) and of K-HTB tungstate rods synthesized in the KCl/AMT/H₂O system with AMT dilution ($c(W) = 0.07$ M in H₂O) (b).

Figure S3. Representative SEM images (scale bar = 1 μm) of Na-HTB tungstate rods ($c(\text{W}) = 0.07 \text{ M}$): (a) after 4 h of hydrothermal treatment, (b) after 18 d of hydrothermal treatment.

Figure S4. Representative SEM images of nanostructured tungstates after 18 d of hydrothermal treatment ($c(\text{W}) = 0.007 \text{ M}$): (a, b) Li-O tungstates, (c, d) Cs-HTB tungstates.