



# High Surface Area Metal Oxides by Two-Phase Gelation from Non-Alkoxide Precursors

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Catalysis from Bench to Market

## Company Profile

- Contract research
- Heterogeneous catalysis, Materials science
- Renewables
- Environmental catalysis
- Hydrogen storage catalysis
- Energy storage, Battery materials
- Custom catalyst and support development
- Lab scale, bench scale and scale up
- Catalyst carrier and solution inventory
- High throughput synthesis and screening
- Partnered with tollers for scaleup, piloting, manufacturing and metal recycling

## SnO<sub>2</sub> by non-alkoxide sol-gel from alcoholic solutions

Sn(OAc) <sub>4</sub>	solvent	gelation agent	aging for	state	calcination	BET	yield
500mg	7.5ml IPA	air humidity	4 days	white dry powder	300C/4h	131 m <sup>2</sup> /g	210mg
500mg	10ml IPA	air humidity	1 week	white dry flakes	280C/2h	148 m <sup>2</sup> /g	217mg
700mg	2.5ml MeOH	air humidity	1 day	glassy gel	300C/4h	145 m <sup>2</sup> /g	304mg
700mg	5ml MeOH	air humidity	1 day	glassy gel	300C/4h	155 m <sup>2</sup> /g	302mg
700mg	10ml MeOH	air humidity	1 day	whitish gel	300C/4h	152 m <sup>2</sup> /g	294mg
700mg	2.5ml MeOH	2.5ml H <sub>2</sub> O	1 day	white gel	300C/4h	155 m <sup>2</sup> /g	289mg
700mg	2.5ml MeOH	2.5ml 10% glyoxylic acid	1day	clear colorless soln	300C/4h	148 m <sup>2</sup> /g	301mg
700mg	2.5ml MeOH	500mg oxalacetic acid	1day	clear yellow soln	300C/4h	130 m <sup>2</sup> /g	346mg
				re-calcined	300C/2h	174 m <sup>2</sup> /g	326mg
				re-calcined	300C/2h	188 m <sup>2</sup> /g	315mg
				re-calcined	300C/2h	177 m <sup>2</sup> /g	314mg
				re-calcined	300C/2h	186 m <sup>2</sup> /g	311mg
				re-calcined	300C/2h	192 m <sup>2</sup> /g	307mg
				re-calcined	300C/2h	178 m <sup>2</sup> /g	306mg
700mg	5ml MeOH	air humidity	1 day	glassy gel	280C/2h	220 m <sup>2</sup> /g	308mg
700mg	5ml MeOH	5ml H <sub>2</sub> O	1 day	white gel	275C/2h	207 m <sup>2</sup> /g	293mg
700mg	2.5ml MeOH	5ml H <sub>2</sub> O	1 day	white gel	275C/2h	203 m <sup>2</sup> /g	292mg
700mg	5ml MeOH	air humidity	1 day	glassy gel	275C/2h	227 m <sup>2</sup> /g	302mg

Typical temperature ramp: 55C/216min ramp/120C/4h hold/1h ramp/300C/4h hold in 50ml vial

Theory: 500mg Sn(OAc)<sub>4</sub> → 212mg SnO<sub>2</sub>; 700mg Sn(OAc)<sub>4</sub> → 297mg SnO<sub>2</sub>

## Mixed Metal Oxides

Precursors	Solvent	Gelation agent	Calcination	BET [m <sup>2</sup> /g]
<b>1g Sb III acetate + 1g Sn IV acetate</b>				
7ml acac	15ml 2.87M ketoglutaric	350C/5h	166	
	400C/2h	167		
	450C/2h	164		
	500C/2h	154		
	550C/2h	149		
<b>0.5g Sb III acetate + 0.5g Sn IV acetate</b>				
10ml formic	10ml 2M ketoglutaric	350C/4h	148	
<b>1g Sb III acetate + 1g Sn IV acetate</b>				
7ml formic	10ml 2M ketoglutaric	350C/4h	121	
5ml formic	10ml 2M ketoglutaric	350C/4h	126	
2.5ml formic	10ml 2M ketoglutaric	350C/4h	135	
2ml formic	2ml H <sub>2</sub> O	350C/4h	129	
2ml formic	10ml H <sub>2</sub> O	350C/4h	140	
1.1ml formic	10ml H <sub>2</sub> O	350C/4h	135	

## SnO<sub>2</sub> by non-alkoxide sol-gel from organic solutions

Generic Recipe:	dissolve metal precursor in organic solvent at RT, add gelation agent, mix by shaking, age the gel, isolate gel by centrifugation or solvent evaporation at RT over 1-5 days, calcine the gel			
Precursor	Solvent	Gelation agent	Calcination	BET [m <sup>2</sup> /g]
1g Sn IV acetate	5ml acac	2ml 2.43M ketoglutaric	350C/5h	135
1g Sn IV acetate	30ml toluene	10ml 1.43M ketoglutaric	350C/5h	163
1g Sn IV acetate	40ml isopropanol	10ml 1.43M ketoglutaric	350C/5h	163
1g Sn IV acetate	20ml MIBK + 3ml acac	7ml 1.43M ketoglutaric	350C/5h	144
1g Sn IV acetate	5ml ethylene glycol	10ml 2.43M ketoglutaric	350C/5h	197
1g Sn IV acetate	5ml ethylene glycol	-	350C/5h	67
1g Sn IV acetate	5ml ethylene glycol	10ml H <sub>2</sub> O	350C/5h	93
1g Sn IV acetate	5ml ethylene glycol	10ml 1M HNO <sub>3</sub>	350C/5h	107
1g Sn IV acetate	10ml glacial acetic	10ml 2.77M ketoglutaric	350C/5h	201
1g Sn IV acetate	10ml acetic/water 1:1	10ml 2.77M ketoglutaric	350C/5h	200
1g Sn IV acetate	20ml acetic/water 1:1	8ml 3.12M ketoglutaric	350C/5h	179
1g Sn IV acetate	5ml formic acid	5ml 2M ketoglutaric	350C/4h	116
1.5g Sn IV acetate	3ml formic acid	7ml 2M ketoglutaric	350C/4h	113
1g Sn IV acetate	1ml formic acid (!)	10ml 2M ketoglutaric	350C/4h	149
0.5g Sn IV acetate	-	10ml 2M ketoglutaric	350C/4h	175
1ml Sn II acac	-	5ml 1.43M ketoglutaric	350C/5h	21
1ml Sn II acac	-	15ml 3.12M ketoglutaric	350C/5h	61
1ml Sn II acac	-	-	450C/2h	50
1g SnCl <sub>4</sub>	-	10ml 2.32M ketoglutaric	400C/5h	52
1g SnCl <sub>4</sub>	-	20ml 2.7M ketoglutaric	350C/4h	161
1g SnCl <sub>4</sub>	-	5ml 50% glyoxylic	350C/4h	20

## Metal Oxides by 2-Phase Gelation from non-alkoxide Precursors

Precursor	Solvent	Gelation agent	Calcination	BET [m <sup>2</sup> /g]
1g In III acetate	12ml acac	10ml H <sub>2</sub> O	350C/5h	72
1g In III acetate	12ml acac	10ml 1.7M ketoglutaric	350C/5h	136
1g In III acetate	12ml acac	10ml 2.87M ketoglutaric	350C/5h	121
			450C/2h	99
1g In III acac	12ml acac	10ml 2.87M ketoglutaric	350C/5h	75
			450C/2h	61
1g In III acac	15ml ethylene glycol	10ml 3.1M ketoglutaric	400C/5h	74
0.5g In III acac	-	10ml 3.1M ketoglutaric	400C/5h	119
1g In III hydroxide	-	10ml 1.7M ketoglutaric	400C/5h	47
1g In III hydroxide	-	10ml 1.7M ketoglutaric	400C/5h	22
0.5g Ni II formate	-	10ml 2.66M ketoglutaric	400C/5h	42
1g Ni II hydroxide	-	10ml 2.7M ketoglutaric	350C/4h	200
0.5g Ru III acac	14ml acac	10ml 1.7M ketoglutaric	350C/5h	99
1g TiO acac	20ml acetic/water 1:1	10ml 3.07M ketoglutaric	400C/5h	137
1g TiO acac	20ml acac	20 H <sub>2</sub> O	400C/5h	101
1g Ga III acac	12ml acac	5ml 1.43M ketoglutaric	500C/1h	87
1g Ga III acac	13ml acac	10ml 1.7M ketoglutaric	500C/2h	78
1g Mn II acac	15ml acac	10ml 2.7M ketoglutaric	350C/4h	73
1g Y III acetate	10ml H <sub>2</sub> O	10ml 2.77M ketoglutaric	400C/5h	215
1g Y III acetate	-	10ml 2.66M ketoglutaric	400C/5h	188
1g Ce III acetate	20ml acac	20ml H <sub>2</sub> O	400C/5h	84
0.5g Ce III acac	10ml formic	10ml H <sub>2</sub> O	350C/4h	102

## Conclusions

- High surface area mixed metal oxides by one- and two-phase gelation and combustion synthesis
- High throughput screening of formulations
- Robotic dispensing of precursors and reagents
- Common, inorganic, non-alkoxide precursors
- Common organic solvents and aqueous gelation agents
- High surface areas achievable for Sn, In, Y, Ni, Ce, Mn, Ti
- Developed shaping recipes of powders into extrudates with remarkably high crush strength