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Design and Control of Lewis Acid Sites in Sn-substituted Microporous Architectures

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Contents

1. Supporting Characterisations

1.1. TG-DTG

TGA-DTG analyses were collected using TA instruments, Q50 TGA model. Typically, ~10 mg of the as-synthesised sample was placed into a platinum pan and loaded to the instrument. Then, the weight% was recorded upon heating to 800 °C at 5 °C/min and in flow of 100 ml/min of compressed air (60% balanced in N_2). In order to identify the species evolved by calcination, ~ 20 mg of each sample was charged into Catlab Microreactor module (Hiden analytical) with a MS detector. The sample was placed into a quartz tube on a bed of glass wall and heated up to 800 °C (5 °C/min) in flow of 10% O_2/He. As a result, MS signals of masses 12, 17, 18 and 44 were recorded.

1.2. MAS NMR experimental conditions.

- **^{119}Sn MAS NMR**

- Pulse sequence: Hahn echo with rotor sequence of 90- τ-180
- Spectrometer: Bruker Avance III HD
- Magnetic frequency: 400.177 MHz
- Relaxation delay: 2.0 s.

- **^{31}P and ^{27}Al MAS NMR**

- Pulse sequence: hpdec for ^{31}P and onepul for ^{27}Al
- Spectrometer: Bruker Avance III HD for ^{31}P and Varian VNMRS for ^{27}Al.
- Magnetic frequency: 161.99 MHz for ^{31}P and 104.199 MHz for ^{27}Al.
- Pulse duration: 4.40 μs for ^{31}P and 1.0 μs for ^{27}Al.
- Recycle delay: 10 s for ^{31}P and 0.2 s for ^{27}Al.

1.3. DR UV/Vis spectroscopy

UV/Vis DRS were collected using UV-Vis 2600 spectrometer with an integrated sphere. Typically, a portion of the calcined sample (*ex situ* calcined and stored in a desiccator under vacuum) was placed into the sample holder. The sample's surface was flattened prior to the measurement and then the %R was recorded as a function of wavelength in the range of 200–800 nm. The %R was then converted to the absorbance using the Kubelka-Munk function. Baseline was corrected by using blank $BaSO_4$ discs before the measurement. For the reduced samples, a portion of the calcined sample was placed and heated in tube furnace in flow of pure H_2 at 400 °C for 2 h, then cooled down to RT in the same atmosphere. The tube containing the sample was sealed well and transferred into a glove box for the preparation purpose (placed in a homemade PTFE sample holder, covered by a quartz window) prior to each measurement. To ensure more protection of the sample and hence reduce the probability of sample's re-oxidation, vacuum grease was used at the edges of the sample holder between the holder and the quartz window, then place into a zipped bag for transfer to the instrument.

1.4. BET surface area (S_{BET}):

S_{BET} was calculated using the BET equation using N_2 Physisorption analysis at 77 K on Quantachrome, Quadrasorb evo model. Prior to the measurement, all samples were degassed for 12 h at 150 °C to 0.1 Pa.

2. Supporting results

2.1. Template removal by calcination

Calcination at 550 °C was given first trail, which is commonly used for removing the SDA (N,N-dicyclohexylmethyl amine) from AlPO-5 based materials. However, this temperature was not enough to completely remove the SDA as can be seen from **Fig. S1 A** below (gray/oily solid powder obtained). So calcination at 700 °C was used to remove the template (**Fig. S1 B**).

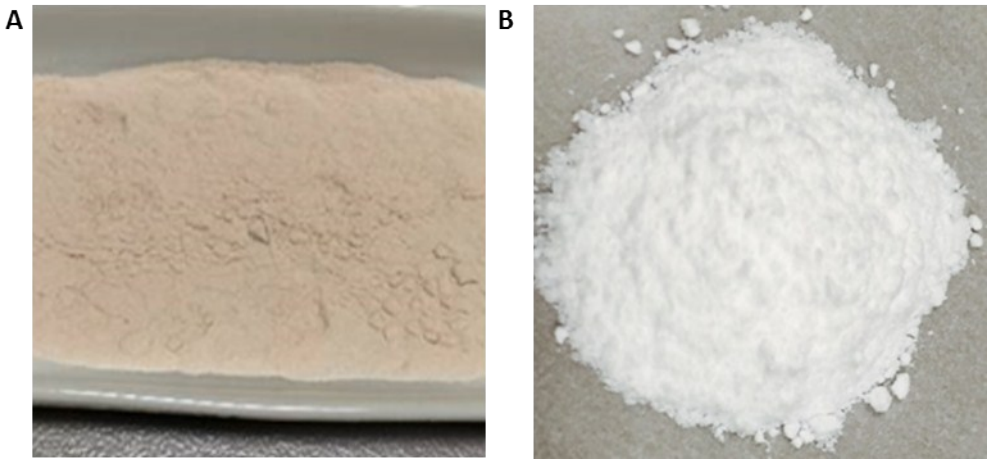

Fig. S 1 The color of 3%Sn AlPO-5 sample after being calcined at **A**) 550 °C and **B**) 700 °C.

2.2. TGA

The removal of the organic template from the as-synthesised materials during their calcination in flow of compressed air as well as their thermal stabilities were studied using TG-DTG analysis. In addition, the evolved species were further traced using a MS detector by monitoring mass 12, 17, 18 and 44 while heating in flow of 10% O_2/He in a distinct experiment. The results are presented in **Fig. S2** and **S3** below for 3%Sn and 6%CoSn AlPO-5 samples, respectively. The weight loss (%) in the temperature window of RT-150 °C is due to the desorption of physisorbed water. The removal of chemisorbed water and/or removal of organic SDA appear at 250–450 °C, while complete combustion of organic SDA residue appears between 500-700 °C. The results showed that the samples are thermally stable up to 800 °C. Based on this, the template was removed by the calcination at 700 °C (5 °C/min) in flow of compressed air.

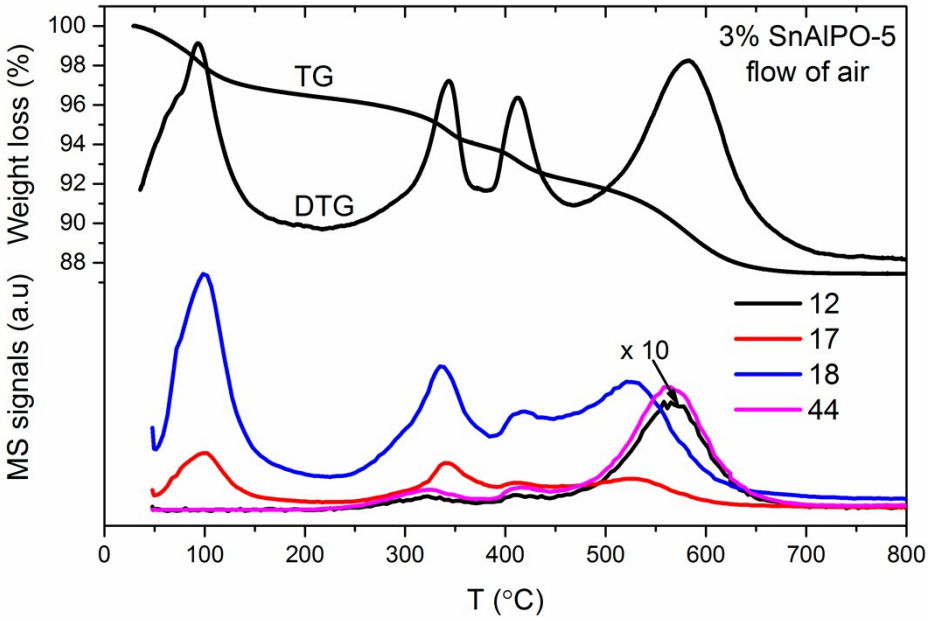

Fig. S 2 TG-DTG (top) and MS signals (bottom) in flow of air while heating up (800 ºC, 5 ºC/min) for the as-synthesised 3% SnAlPO-5 sample, as indicated.

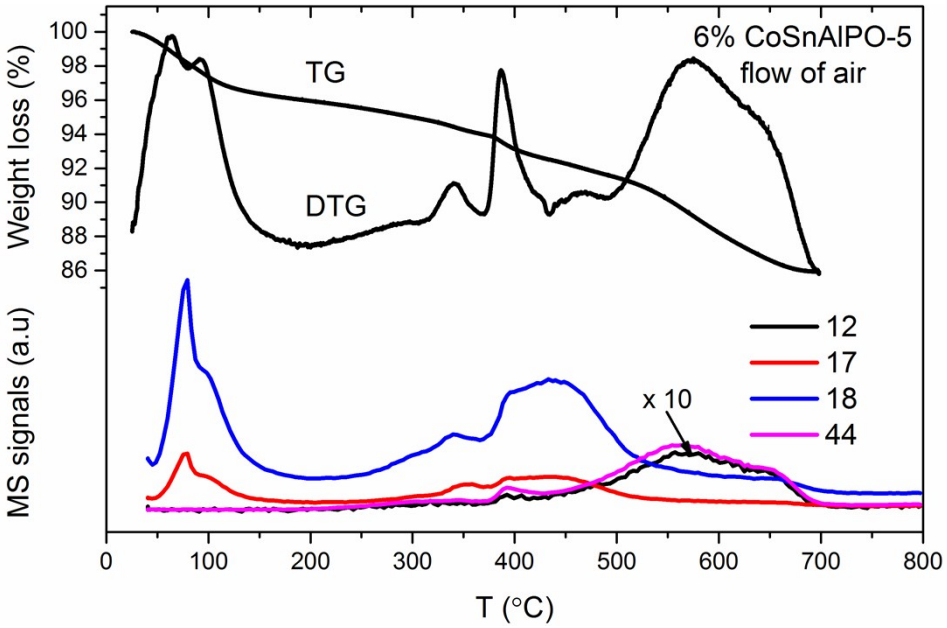

Fig. S 3 TG-DTG (top) and MS signals (bottom) in flow of air while heating up (800 ºC, 5 ºC/min) for the as-synthesised 6% CoSnAlPO-5 sample, as indicated.

2.3. Index of XRD patterns

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AlPO-5-700C sample

Initial values : (Refinement keys on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0.00	1.54060	13.7074	13.7074	8.3706	90.000	90.000	120.000	1362.1
0	0	1	0	1	0	0	0	

Final values : (Standard errors on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0.00	1.54060	13.7085	13.7085	8.3707	90.000	90.000	120.000	1362.3
0.00	0.00000	0.0143	0.0000	0.0012	0.000	0.000	0.000	

H	K	L	2T(Obs)	2T-Zero	2Th(Cal)	Dif
0	1	0	7.4600	7.4600	7.4404	0.0196
1	1	0	12.9200	12.9200	12.9054	0.0146
0	2	0	14.9400	14.9400	14.9124	0.0276
1	2	0	19.7800	19.7800	19.7696	0.0104
0	0	2	21.2000	21.2000	21.2112	-0.0112
1	2	1	22.4800	22.4800	22.4634	0.0166
1	1	2	24.9400	24.9400	24.9069	0.0331
2	2	0	25.9800	25.9800	25.9782	0.0018
1	2	2	29.1400	29.1400	29.1539	-0.0139
0	4	0	30.0600	30.0600	30.0851	-0.0251
2	2	2	33.7800	33.7800	33.7763	0.0037
1	4	0	34.5800	34.5800	34.5954	-0.0154
0	4	2	37.0800	37.0800	37.1047	-0.0247
1	2	3	37.9600	37.9600	37.9423	0.0177

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3%Sn-700C sample

Initial values : (Refinement keys on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0.00	1.54060	13.7703	13.7703	8.3776	90.000	90.000	120.000	1375.7
0	0	1	0	1	0	0	0	

Final values : (Standard errors on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0.00	1.54060	13.7703	13.7703	8.3776	90.000	90.000	120.000	1375.7
0.00	0.00000	0.0258	0.0000	0.0027	0.000	0.000	0.000	

H	K	L	2T(Obs)	2T-Zero	2Th(Cal)	Dif
0	1	0	7.3600	7.3600	7.4070	-0.0470
1	1	0	12.8000	12.8000	12.8472	-0.0472
0	2	0	14.8200	14.8200	14.8451	-0.0251
1	2	0	19.6600	19.6600	19.6800	-0.0200
0	0	2	21.1400	21.1400	21.1935	-0.0535
0	3	0	22.3200	22.3200	22.3468	-0.0268
2	2	0	25.8600	25.8600	25.8596	0.0004
1	2	2	29.0400	29.0400	29.0787	-0.0387
0	4	0	29.9800	29.9800	29.9470	0.0330
2	2	2	33.7200	33.7200	33.6715	0.0485
2	3	1	34.4600	34.4600	34.4576	0.0024
0	4	2	37.0400	37.0400	36.9794	0.0606
1	2	3	37.8800	37.8800	37.8697	0.0103

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6%CoSn-700C sample

Initial values : (Refinement keys on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0.00	1.54060	13.7623	13.7623	8.3631	90.000	90.000	120.000	1371.8
0	0	1	0	1	0	0	0	

Final values : (Standard errors on 2nd line)

Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0.00	1.54060	13.7626	13.7626	8.3631	90.000	90.000	120.000	1371.8
0.00	0.00000	0.0311	0.0000	0.0029	0.000	0.000	0.000	

H	K	L	2T(Obs)	2T-Zero	2Th(Cal)	Dif
0	1	0	7.3800	7.3800	7.4111	-0.0311
1	1	0	12.8400	12.8400	12.8545	-0.0145
0	2	0	14.8400	14.8400	14.8535	-0.0135
1	2	0	19.6600	19.6600	19.6911	-0.0311
0	0	2	21.1400	21.1400	21.2305	-0.0905
0	3	0	22.3400	22.3400	22.3595	-0.0195
1	1	2	25.0000	25.0000	24.8965	0.1035
2	2	0	25.8600	25.8600	25.8743	-0.0143
1	2	2	29.0800	29.0800	29.1139	-0.0339
0	4	0	29.9800	29.9800	29.9642	0.0158
2	2	2	33.7200	33.7200	33.7072	0.0128
2	3	1	34.4800	34.4800	34.4815	-0.0015
0	4	2	37.0800	37.0800	37.0158	0.0642
1	2	3	37.9000	37.9000	37.9248	-0.0248

Table S1: Cell parameters extracted from XRD analysis.

Sample	Cell parameters (XRD)	
	a (Å)	c (Å)
AlPO-5-700C	13.71	8.37
3%Sn-700C	13.77	8.38
6%CoSn-700C	13.76	8.36

2.4. BET surface area (S_{BET})

Table S2: S_{BET} ($m^2.g^{-1}$) values extracted from N_2 Physisorption analysis.

Sample	S_{BET} ($m^2.g^{-1}$)
AlPO-5-700C	345 (±5)
3%Sn-700C	399 (±5)
6%CoSn-700C	168 (±5)

3. References

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