# Improved lifetime and stability of copper species in hierarchcial, copperincorporated CuSAPO-34 verified by catalytic model reactions

Guro Sørli, <sup>a§</sup> Muhammad Mohsin Azim <sup>a‡</sup>, Magnus Rønning<sup>b±</sup>, and Karina Mathisen <sup>\*a†</sup>

## A. Initial testing of mesoSDAs

Copper(II) acetate (0.03 M, 20 ml, Fluka Chemika) was stirred together with the chosen SDA (~ 5 ml) and transferred to a 50-ml Teflon lined stainless-steel autoclave overnight at 150°C. SDAs are typically amines causing the end solution to be basic (ph ~ 7-8), hence this procedure was also done by adjusting the pH to approximately 4-5 using ortho-phosphoric acid ( $H_3PO_4$ , 5 M, Merck). The plain copper(II) solution was also heated overnight in the plain form and the coherent acidic form. The plain copper(II) acetate solution contained black precipitate after a night in autoclave at 150°C unless it was acidified which remained its pale blue color. This was also in accordance with the non-acidified copper(II)-SDA combinations which all became black or contained black precipitate without being acidified. This concludes that presence of the hydroxide (-OH) ion is not favorable when avoiding autoreduction of copper(II).

### The following mesoSDA were included:

Myristyltrimethylammonium bromide (TTAB, 98%, Sigma-Aldrich), cetyltrimethylammonium bromide (CTAB, 98%, Sigma-Aldrich), behenic acid (99%, Sigma-Aldrich), Trimethoxy(octadecyl)silane (TMOS, technical grade, Sigma-Aldrich), sodium dodecylbenzenesulfonate (SDBS, technical grade, Aldrich), Pluronic<sup>®</sup> P-123 (~5,800 g/mol, Sigma-Aldrich), polyethylene oxide (PEO, ~100,000 g/mol, Sigma-Aldrich), Dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (DMOCI, 42% in methanol, Sigma-Aldrich), D-(+)-glucose monohydrate (glucose, analytical specification of Ph. Eur, Sigma-Aldrich), Pluronic<sup>®</sup> F-127 (~ 12,600 g/mol, Sigma-Aldrich). CTAB was also ion exchanged through an Amberlite resin (IRN-78, Alfa Aesar) column to create cetyltrimethylammonium hydroxide (CTAOH) which was also included in the parameter study as a mesoSDA.

#### B. Tables

**Table S1** Overview of change in synthesis parameters for the synthesis of hierarchical CuSAPO-34 with the basis in the following molar ratios: 1 Al: x P : 0.5 Si : 0.05 Cu: y TEAOH : z 2<sup>nd</sup> microSDA : 0.0004 F127 : 30 H<sub>2</sub>O. Crystallization times were kept constant at 120 hours unless otherwise stated employing a crystallization temperature of 150 °C. Green is used to highlight combinations that provided phase pure CHA and blue is for the conventional CuSAPO-34.

	Ρ·ΔΙ	Micro	SDA:Al ratio	Type of 2 <sup>nd</sup>	pH of		
Sample name	ratio (x)	ΤΕΑΟΗ (γ)	2 <sup>nd</sup> microSDA (z)	microSDA	synthesis	Phase	
					gel		
<sup>1,2</sup> CuSAPO-34	1.2	1	-	-	6.3	СНА	
1	1	0.5	-	-	3.0	AFI	
2	1	0.6	-	-	3.5	CHA + AFI	
3	1	0.7	-	-	4.0	CHA + AFI	
4	1	0.8	-	-	6.0	Amorph	
5	1	0.9	-	-	6.5	Amorph	
6	1	1	-	-	6.9	CHA + unidentified	
7	1.1	1	-	-	6.8	Amorph	
8	1.2	1	-	-	6.4	СНА	
9	1	0.5	0.5	TMAOH		SOD	
10	1	0.5	0.1	TPAOH	3.6	AFI	
11	1	0.5	0.2	TPAOH	4.5	AFI	
12	1	0.5	0.3	TPAOH	5.9	AFI	
13	1	0.5	0.4	ТРАОН	6.5	CHA + AFI	
14	1	0.5	0.5	ТРАОН	6.7	СНА	
15	1	0.6	0.4	ТРАОН	6.7	СНА	
16	1	0.7	0.3	ТРАОН	6.6	СНА	
17	1	0.8	0.2	TPAOH	6.6	СНА	
18	1	0.9	0.1	TPAOH	6.7	СНА	

<sup>1</sup>Synthesized without F127

<sup>2</sup> Crystallization time 144 hours

Table S2 Overview of physical properties provided from the t-plot method (N<sub>2</sub> adsorption) in addition to pore volumes. Additional ICP-MS results are also given.

Sample	<sup>a</sup> t-plot (m <sup>2</sup> /g)	<sup>a</sup> Pore vo	lume (cm³/g)			_
	Micro/meso area	Micro	<sup>b</sup> Meso	_ °(Al+P)/Si	۶P:Al	N ac ti⁄
CuSAPO-34	252/40	0.13	0.07	25	0.8	_
H-CuSAPO-34	299/36	0.15	0.06	13	0.8	
						_

between total pore volume and micropore volume

<sup>c</sup> Results from ICP-MS

**Table S3** EXAFS refinements of the first shell for the references to obtain AFAC from each reference. The coordination numbers are extracted from references; Cu2O [5], CuO [5], and Cu tutton [7] and was not refined. The AFAC and the Debye-Waller were decorrelated, where the Debye-Waller was stepwise changed and kept constant, while the EF, R and AFAC were refined. This was done both for  $k^2$  – and  $k^3$ -weighting, and AFAC chosen is given by the best fit. For all references the best fit was found for  $k^3$ -weighting.

Sample	Shell	EF	2σ² (Ų)	Ν	R (Å)	R%	FI	Δk	AFAC
Cu <sub>2</sub> O	Cu-O	-9.7(5)	0.0075	2	1.857(5)	34.30	0.00077	2-15	0.79(4)
CuO	Cu-O	-9.2(6)	0.006	4	1.959(5)	38.86	0.00086	2-15	0.70(4)
Cu tutton	Cu-O	-5.2(5)	0.012	4	1.981(6)	30.04	0.00073	2-15	0.81(4)

Table S4 EXAFS refinements of spent samples after lifetime study in selective propene oxidation, where the copper species in CuSAPO-34 are dominated by the CuO contribution, while H-CuSAPO-34 can only be fitted with the first shell O-contribution at 1.94 Å. Both refinements were done using a k<sup>3</sup>-weighting.

Sample	Shell	EF	$2\sigma^2$ (Å <sup>2</sup> )	N	R (Å)	R%	FI	Δk	AFAC
CuSAPO-34	Cu-O	-6.5(5)	0.007(1)	4.2(3)	1.96(4)	33.95	0.00062	2-15	0.70
	CuCu		0.027(7)	7(2)	2.94(1)				
	CuCu		0.009(4)	2(1)	3.13(1)				
H-CuSAPO-34	Cu-O	-5.4(7)	0.016(3)	3.1(3)	1.935(8)	40.62	0.00121	2-13	0.79

The employed AFAC are derived from CuO (CuSAPO-34) and Cu<sub>2</sub>O (H-CuSAPO-34) as the latter contains contribution of Cu<sup>+</sup> seen in the XANES.

### C. Figures



**Fig. S1** As prepared samples compared to reference x-ray diffractograms to verify phase purity; Cu0 (PDF 00-004-0836, ICDD, 2020) in pink, Cu2O (PDF 00-005-066, ICDD, 2020) in blue, Cu(OH)2 (PDF 04-009-4366, ICDD, 2020) in green, and CuO (PDF 00-041-0254, ICDD, 2020) in orange compared to the CHA diffractograms of as prepared samples; CuSAPO-34 (only TEAOH with increased phosphorous addition) and H-CuSAPO-34 (combination of TEAOH and TPAOH as microSDAs). Reflections originating from Cu(OH)<sub>2</sub> are scaled 5 times for exemplification.



Fig. 52 FITR spectra from CO adsorption showing OH-region from 3800-3100 cm<sup>-1</sup> as well as CO-region in-between 2250- 2050 cm<sup>-1</sup> (left). The area underneath bands found in OH-region is integrated and used to calculate the acid density (right). Spectra a are CO loaded until approximately 0.85 mbar and I equals vacuum spectra. The acid strength is given by the OH-shift when comparing spectra a and I.



Fig. S3 Adsorption isotherms from N<sub>2</sub> adsorption showing H4 isotherm for both H-CuSAPO-34 (orange) and CuSAPO-34 (blue). The Pore Size Distribution (PSD) showing the tensile strength effect (TSE) at 3.8 Å.



Fig. S4 XANES of selected model compounds;  $Cu^{0}$  (a),  $Cu_{2}O$  (b), CuO (c),  $Cu(OH)_{2}$  (d) and  $Cu^{2+}$  tutton salt (e).



Fig. S5 EXAFS and FT-EXAFS of the as prepared CuSAPO-34 as prepared together with Cu<sup>2+</sup> model compounds of relevance. The Cu<sup>2+</sup> tutton salt is only shown for the XANES as the Cu-O-Cu interaction seen for CuO and Cu(OH)<sub>2</sub> is of particular interest in the chi-curve and FT-EXAFS.



Fig. S6 EXAFS and FT-EXAFS of the H-CuSAPO-34 as prepared together with Cu<sup>2+</sup> model compounds of relevance.



**Fig. S7** Decorrelation of AFAC at  $k^3$ -weighting (orange) and  $k^2$ -weighting (blue) for the refinement of the Debye-Waller factor ( $2\sigma^2$ ). AFAC of the respective sample is the intersection of the  $k^2$  and  $k^3$  weighted relation between AFAC and  $2\sigma^2$ .



Fig. S8 EXAFS refinements of CuSAPO-34 (a as prepared, b calcined) and H-CuSAPO-34 (c as prepared, d calcined)



Fig. S9 Fourier filtering the second shell around 3 Å for the conventional CuSAPO-34 concluding a T-atom as the most plausible contributor.



Fig. S10 Fourier filtering the second shell around 3 Å for the hierarchical H-CuSAPO-34 concluding a T-atom as the most plausible contributor.



Fig. S11 Employing propene as reductant in selective reduction of NO reveals that H-CuSAPO-34 and CuSAPO-34 are both active with accessible  $Cu^{2*}$ , but the activity is somewhat dependent on the propene content in reaction feed (right). For comparison the mesoporous  $Cu/ZrO_2$  is also given (black).



Fig. S12 LCF results on the spent CuSAPO-34 and H-CuSAPO-34 showing contribution of single site Cu<sup>2+</sup> and CuO<sub>x</sub> in various amounts depending on sample. The obtained R-factors from Athena are listed on the respective columns.