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The role of copper speciation in the low temperature oxidative upgrading of short chain alkanes over Cu/ZSM-5 catalysts

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S1.1 Hydrothermal synthesis of Silicalite-1

Silicalite-1 was synthesised according to the following procedure; tetrapropylammonium hydroxide (20 wt % in H_2O, 50.8 g, corresponding to 49.9 mmoles TPAOH) was stirred vigorously (25 ^oC, 1 h). To this solution tetraethylorthosilicate (10.24 g, 49.4 mmoles) was added drop wise. The resulting gel was homogenised (60 ^oC, 5 h) prior to crystallisation in a Teflon lined stainless steel Parr autoclave (175 ^oC, 48 h). The as synthesised material was later recovered by filtration, washed with deionised water (1 L) and dried in air (110 ^oC, 16 h). The dried sample was then ground in a pestle and mortar, prior to heat treatments (550 ^oC, 8 h, 1 $^oC\ min^{-1}$) in a flow of N_2 (5 h) followed by (10 h) in flowing air to remove the template.

S1.2 Ethene oxidation experiments

Ethene oxidation studies followed the same methodology outlined in the experimental section, but were conducted in a 100 mL Teflon lines Parr autoclave reactor at a total pressure of 10 bar (5% C_2/H_4/ N_2, 40 mL gas volume).

Table S1 Catalytic data for ethene oxidation catalysed by ZSM-5 catalysts at 50 and 70 °C

Entry	Catalyst	Temp °C	Total Products / µmol	Products / µmol									H_2O_2 converted / %
				CH_3COOH	EtOH	CH_3CHO	EtOOH	GlyOOH	MeOOH	MeOH	HCOOH	CO_x	
1	H-ZSM-5 (30)	50	10.2	0	0.9	0.6	2.0	0	2.6	1.4	1.7	1.0	5.9
2	H-ZSM-5 (30)	70	61.1	2.57	1.1	0.6	3.4	0	3.7	2.0	42.6	5.1	16.4
3	2.5% Cu/ZSM-5 (30)	50	10.3	0	0.6	0.6	4.6	0	3.1	0.3	0.0	1.1	6.1
4	2.5% Cu/ZSM-5 (30)	70	23.7	2.0	0.9	2.6	3.7	0	4.6	0.6	4.6	4.7	18.5
5	1.25% Fe/ZSM-5 (30)	50	189.6	4.9	0.9	0.6	0.6	5.7	0.9	4.9	154.6	16.5	36.1
6	1.25% Fe/ZSM-5 (30)	70	540.7	7.4	0	0	0.0	12.3	0	12.6	338.0	170.4	91.6
7	1.25% Fe 1.25% Cu/ZSM-5 (30)	50	83.9	30.0	0.3	0.3	0.0	2.3	1.1	15.4	27.4	7.1	31.0
8	1.25% Fe 1.25% Cu/ZSM-5 (30)	70	410.8	71.4	0.6	0.0	0.0	10.3	0.0	15.1	178.3	135.1	84.8

Test conditions; 56 mg catalyst, reaction volume = 20 ml, [H_2O_2] = 0.25 M (5000 µmol), 0.5 h, Gas phase volume = 40 ml, P (5% C_2H_4/ N_2) = 10 bar

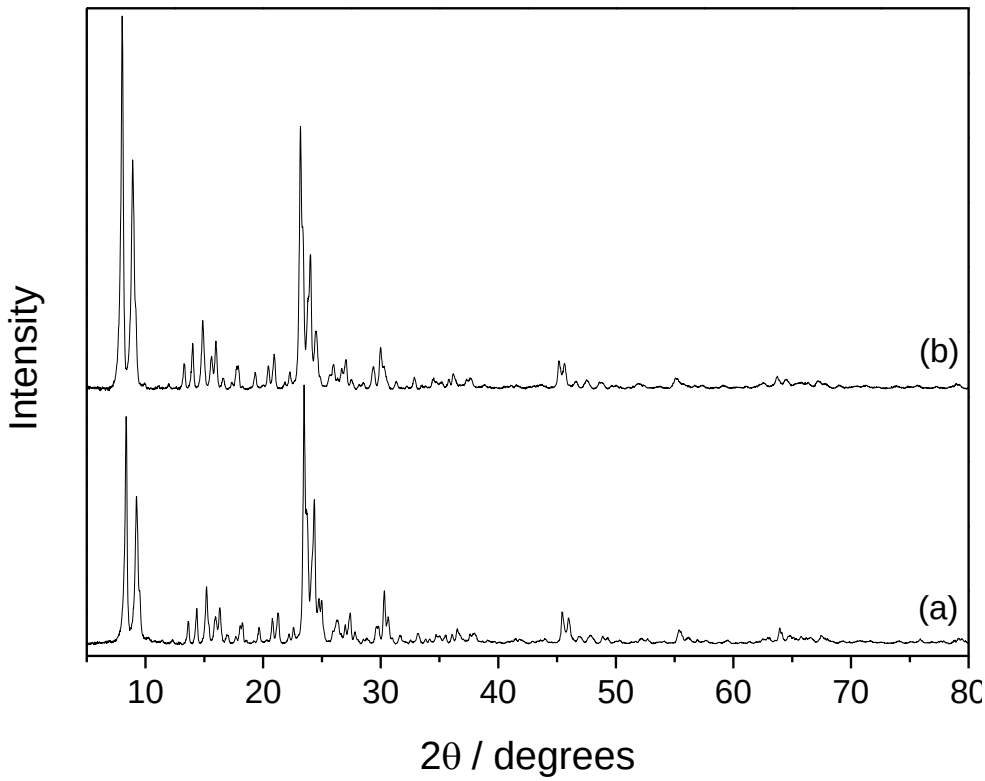

Figure S1 XRD patterns for (a) Silicalite-1 prepared by hydrothermal synthesis and (b) 2.5% Cu/Silicalite-1 prepared by CVI.

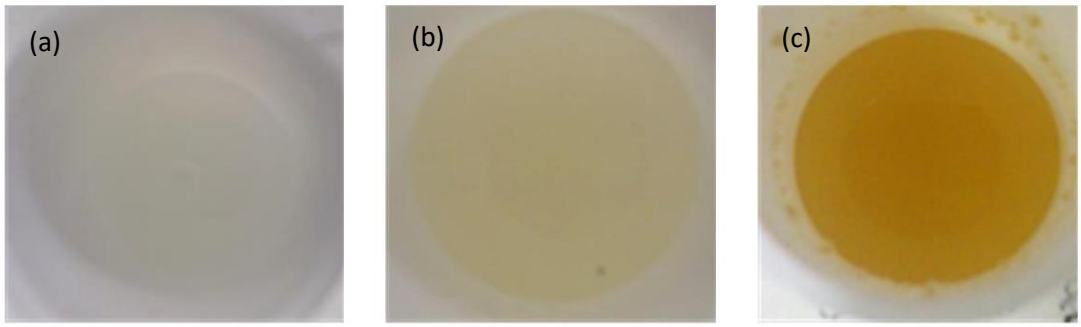

Figure S2 Photographs of 2.5% Cu/ZSM-5 catalysts (suspended in reaction solution – housed within PTFE liner) following methane oxidation reactions where SiO_2/Al_2O_3 = (a) 23, (b) 30 and (c) 280. Test conditions; 27 mg catalyst, 0.5 h, P(CH_4) = 30 bar (0.03 mol), 50 ^oC, 1500 rpm, [H_2O_2] = 0.5 M (5000 µmol).

Table S2 Physical properties of Cu/ZSM-5 (23) catalysts as determined through N_2 adsorption studies.

Entry	Cu loading / wt. %	[a] Total surface area / m^2g^{-1}	$V_{micropore}$ / cm^3g^{-1}
1	0	423.5	0.168
2	0.4	359.9	0.143
3	1.25	338.8	0.121
4	2.5	308.7	0.101
5	5.0	259.5	0.091

[a] Surface area determined from nitrogen adsorption measurement using the BET equation.

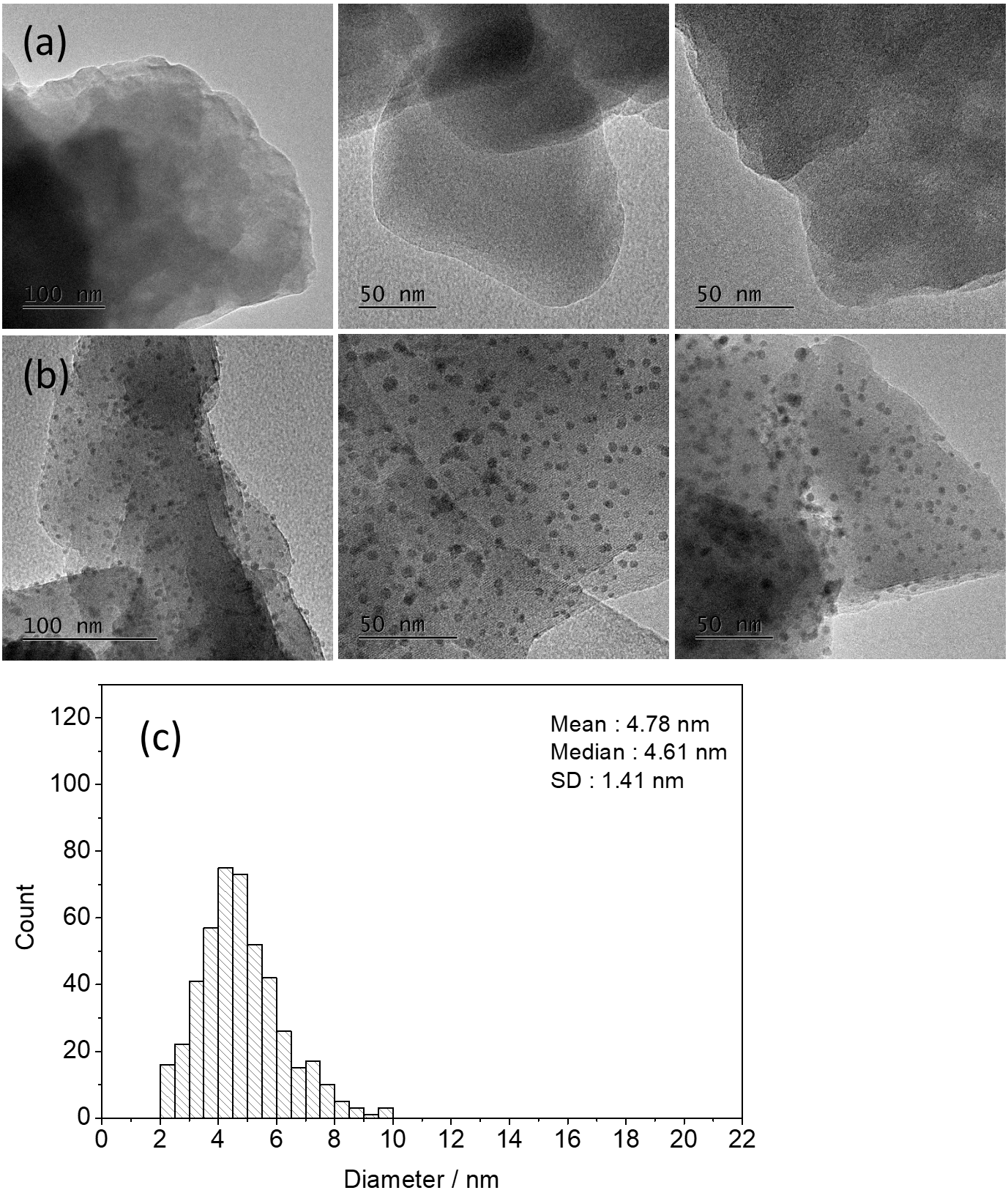

Figure S3 Representative transmission electron micrographs for (a) 0.4 wt% Cu / ZSM-5 (23) and (b) 5 wt% Cu/ZSM-5 (23). Particle size distribution (c) for 5 wt.% Cu/ZSM-5 (23)

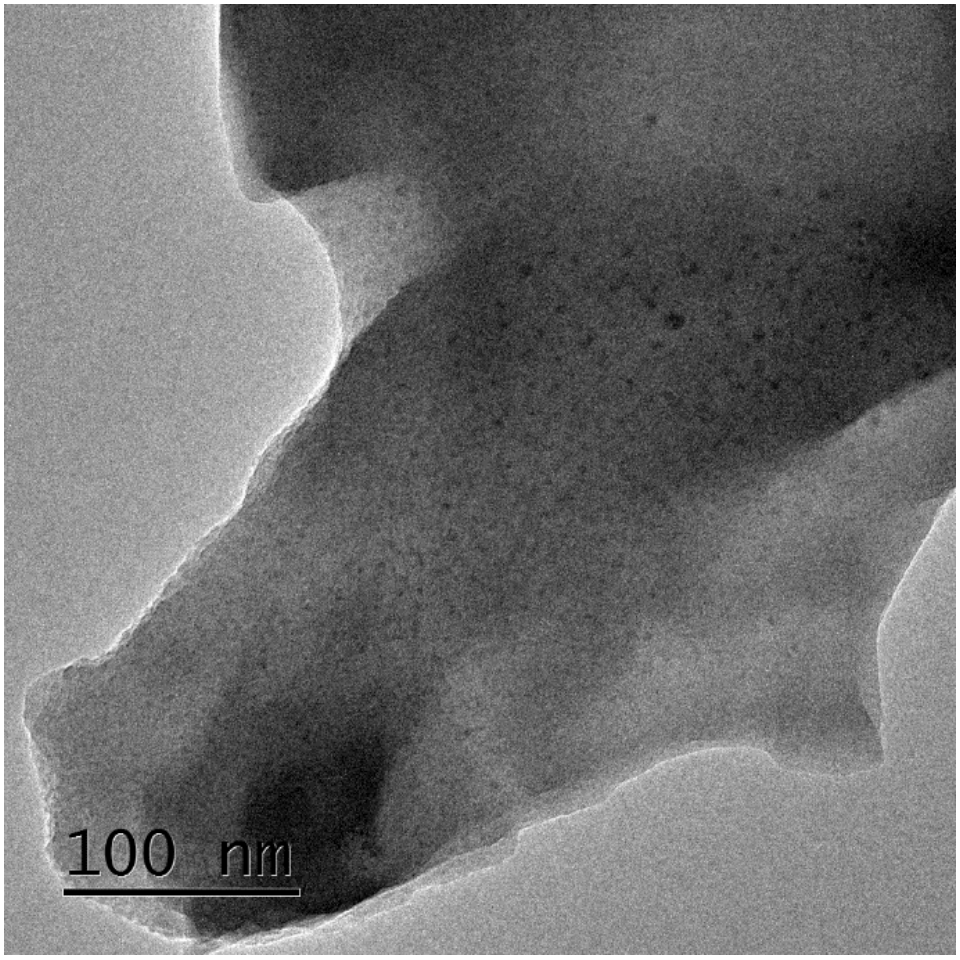

Figure S4 Transmission electron micrograph showing 0.4 wt% Cu / ZSM-5 (23) following prolonged electron beam exposure

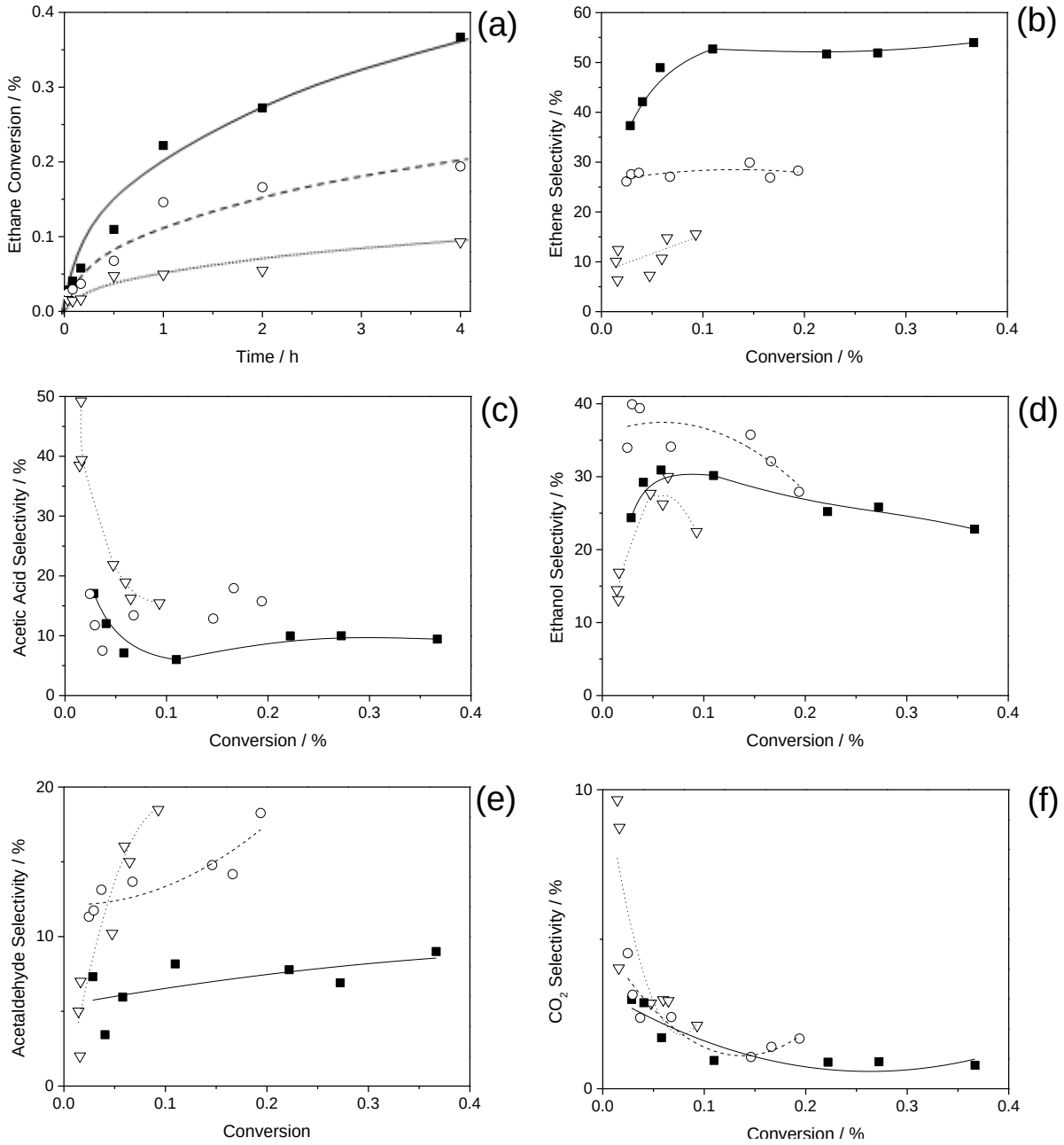

Figure S5 Ethane oxidation time on line analyses (a) of 2.5 wt % Cu/ZSM-5 catalysts where SiO_2/Al_2O_3 = ■ 23, ○ 30, ▽ 280 and corresponding conversion vs selectivity plots for major reaction products; (b) ethene, (c) acetic acid, (d) ethanol, (e) acetaldehyde and (f) CO_2