

Liquid-phase $\text{Cu}(\text{acac})_2/\text{ZnEt}_2$ Syngas Conversion Catalysts: Investigations by Copper and Zinc K-edge EXAFS

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Cu K-edge EXAFS studies on syngas conversion catalysts, generated by the reaction of $\text{Cu}(\text{acac})_2$ (acac = acetylacetonato) with ZnEt_2 at room temp., reveal the presence small Cu metal particles (ca. 10–25 Å) in solution; Zn K-edge studies suggest the formation of oligomeric Zn species with oxygen present in the first coordination sphere.

Liquid-phase catalysts prepared by the reduction of $\text{Co}(\text{acac})_2$ or $\text{Mn}(\text{acac})_2$ with AlEt_3 have been reported to be selective towards the synthesis of $\text{C}_2\text{--C}_6$ alkenes from CO and H_2 ,^{1–3} but despite numerous catalytic studies, it remains unclear as to whether these catalysts are truly homogeneous in nature or whether they are in fact much more complex systems containing metallic clusters, more akin to some heterogeneous systems. More recently, Simon⁴ has demonstrated the activity of liquid phase reduced-Cu/oxidised-Zn systems in the production of oxygenated compounds from syngas under pressure. These catalysts are prepared by the addition of ZnEt_2 to $\text{Cu}(\text{acac})_2$ and excess buta-1,3-diene in benzene at room temp.; the resulting homogeneous red/brown solution, when treated under 60 atm of H_2/CO at 260 °C, produces ethanol with ca. 40–60% molar selectivity.⁴ Simon *et al.* proposed that buta-1,3-diene was necessary to stabilise or solubilise Cu^0 (via a π -allyl intermediate) formed during the reduction of $\text{Cu}(\text{acac})_2$ with ZnEt_2 : in the absence of butadiene, copper

precipitates were observed. We now report EXAFS results† which probe directly the coordination spheres of both the Cu and the Zn components in these precursor mixtures. Our studies show that the apparently homogeneous $\text{Cu}(\text{acac})_2/\text{ZnEt}_2$ /buta-1,3-diene solution is in fact a mixture of colloidal copper and oligomeric Zn species.

The Cu K-edge EXAFS of a dilute solution of $\text{Cu}(\text{acac})_2$ and ZnEt_2 in benzene (1 mmol dm^{-3} in Cu; Cu:Zn = 1:1) is shown in Fig. 1. Analysis reveals backscattering shells due to Cu at 2.50, 3.55, 4.38 and 5.22 Å, consistent with an *fcc* local structure at Cu. The interatomic distances are comparable to those derived from the EXAFS of Cu foil (Table 1) but the refined coordination numbers for the 4 shells (8.4, 3.6, 8.0 and 8.4) are significantly lower than those of bulk Cu. The Cu K-edge EXAFS of $\text{Cu}(\text{acac})_2$, buta-1,3-diene and ZnEt_2 in benzene was of poorer quality, but analogous results were observed; a first coordination sphere ca. eight Cu atoms was clearly identified. Parallel experiments using DMF as the solvent [$\text{Cu}(\text{acac})_2$ was found to have limited solubility in a range of solvents¹⁰] gave similar results: DMF solutions of $\text{Cu}(\text{acac})_2/\text{ZnEt}_2$ (10 mmol dm^{-3} Cu; Cu:Zn = 1:1), with and without buta-1,3-diene, were also found to contain small Cu metal particles. The Cu K-edge EXAFS-derived structural parameters are summarised in Table 1. Reduced coordination numbers (20%) are again noted in comparison to bulk Cu metal.

X-Ray absorption spectroscopy has been employed extensively in the characterisation of small metal particles in heterogeneous systems¹¹ but few reports concerning the application of the technique to the study of metal aggregates in

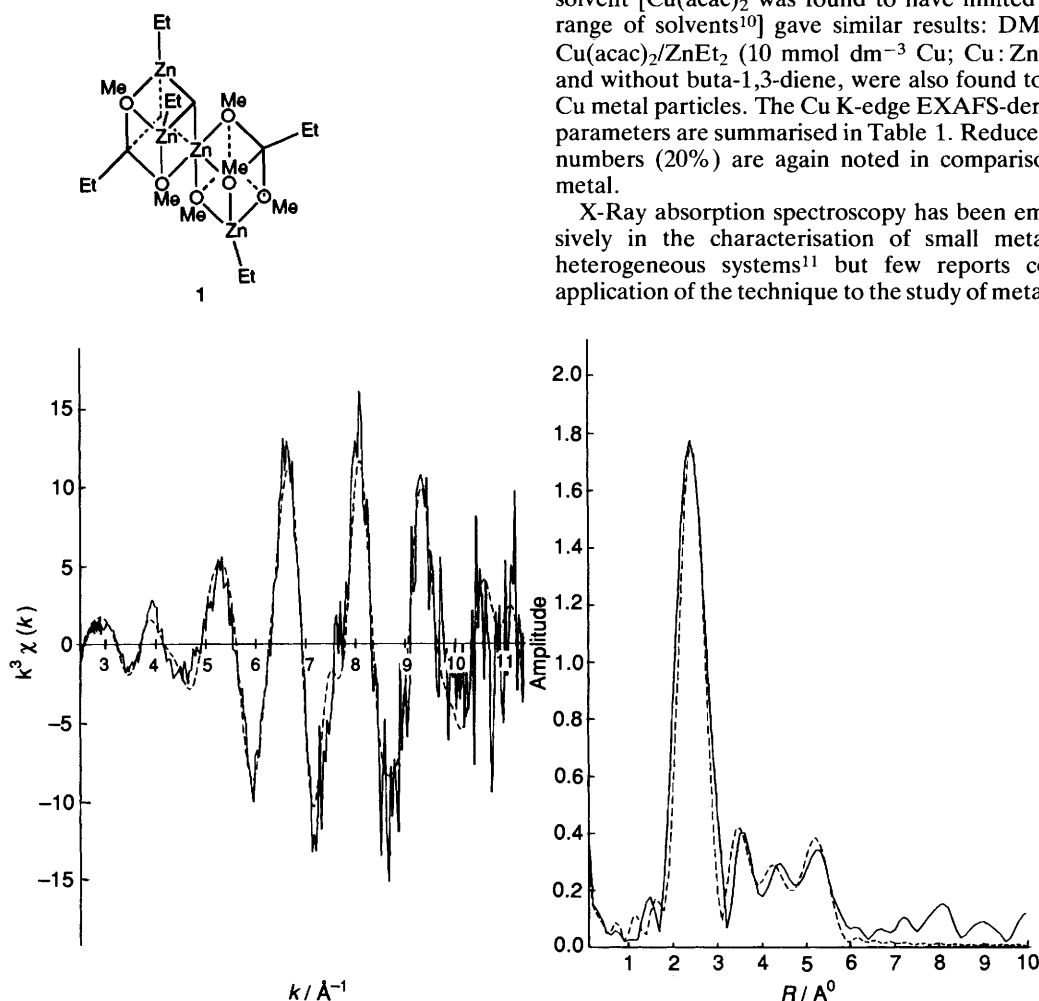


Fig. 1 The Cu K-edge k^3 -weighted EXAFS and Fourier transform, phase-shift corrected for copper, of $\text{Cu}(\text{acac})_2/\text{ZnEt}_2$ in benzene (1 mmol dm^{-3} Cu; 1:1 Cu:Zn) at room temp. (—) Experiment and (---) spherical wave theory.

Table 1 Cu and Zn K-edge EXAFS-derived structural parameters for $\text{Cu}(\text{acac})_2/\text{ZnEt}_2$ and $\text{MeOH}/\text{ZnEt}_2$ in various solvents at room temp.

Sample	K-edge ^a	Shell	CN	R/Å	$2\sigma^2/\text{Å}^{2b}$	R-factor (%)
(i) Cu foil	Cu	Cu	12	2.53	0.016	19.9
		Cu	6	3.55	0.026	
		Cu	24	4.39	0.023	
		Cu	12	5.07	0.021	
(ii) $\text{Cu}(\text{acac})_2/\text{ZnEt}_2/\text{C}_4\text{H}_6/\text{DMF}$	Cu	Cu	10.1	2.52	0.017	24.8
		Cu	5.8	3.54	0.029	
		Cu	20.4	4.38	0.029	
		Cu	10.1	5.06	0.029	
	Zn	O	4.2	1.97	0.018	26.4
		O	2.5	2.19	0.018	
		Zn	4.1	3.19	0.018	
	C/O	5.9	4.44	0.016		
(iii) $\text{Cu}(\text{acac})_2/\text{ZnEt}_2/\text{DMF}$	Cu	Cu	9.9	2.51	0.017	20.7
		Cu	5.1	3.51	0.034	
		Cu	18.3	4.37	0.028	
	Zn	Cu	9.9	5.05	0.028	
		O	2.7	1.96	0.021	25.2
		C	2.8	2.90	0.030	
		Zn	0.7	3.11	0.036	
	C	3.5	3.90	0.028		
(iv) $\text{Cu}(\text{acac})_2/\text{ZnEt}_2/\text{benzene}$	Cu	Cu	8.4	2.50	0.020	37.6
		Cu	3.6	3.55	0.016	
		Cu	8.0	4.38	0.025	
		Cu	8.4	5.22	0.014	
(v) $\text{MeOH}/\text{ZnEt}_2/\text{heptane}$	Zn	O	2.5	1.94	0.021	16.9
		O	1.3	2.17	0.020	
		Zn	2.1	3.04	0.028	
		O	1.6	3.44	0.016	

^a For Cu K-edge spectra, AFAC = 0.79 and VPI = -5.0 eV. E_0 values for samples (i)–(iv) are 11.7, 11.8, 13.1 and 31.7 eV respectively; for Zn K-edge spectra, AFAC = 0.85. VPI values for samples (ii), (iii) and (v) are -2.0, -2.6 and -1.8 eV respectively. E_0 values for samples (ii), (iii) and (v) are 15.7, 18.2 and 14.8 eV respectively. ^b Debye-Waller factor. σ = root mean square internuclear separation.

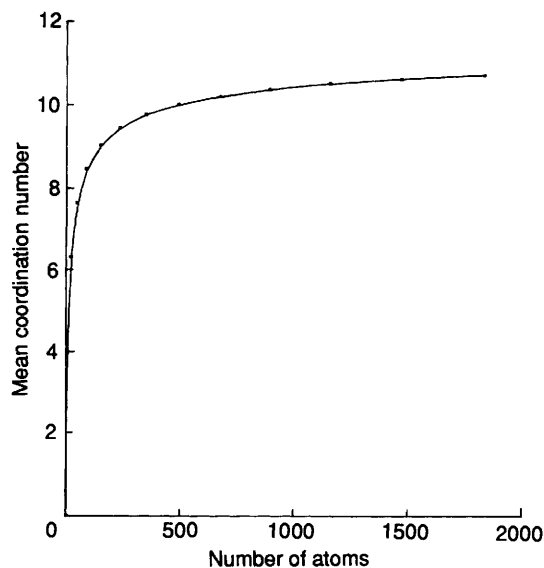


Fig. 2 Plot of mean coordination number vs. number of atoms, calculated for *fcc* copper crystals.¹⁴ For an atom length m , the mean coordination number is given by,

$$\{24 + 84(m - 2) + 72 \sum_{i=1}^{m-3} i + 12[2 \sum_{i=1}^{m-3} i^2 + (m - 2)^2]\} / \{2 \sum_{i=1}^{m-1} i^2 + m^2\}.$$

corner sites, coordination number 4, contribute 6 atoms; edge sites, coordination number 7, contribute $12(m - 2)$ atoms; face sites, coordination number 9, contribute $8 \sum_{i=1}^{m-3} i$ atoms; bulk sites, coordination number 12, contribute $2 \sum_{i=1}^{m-3} i^2 + (m - 2)^2$.

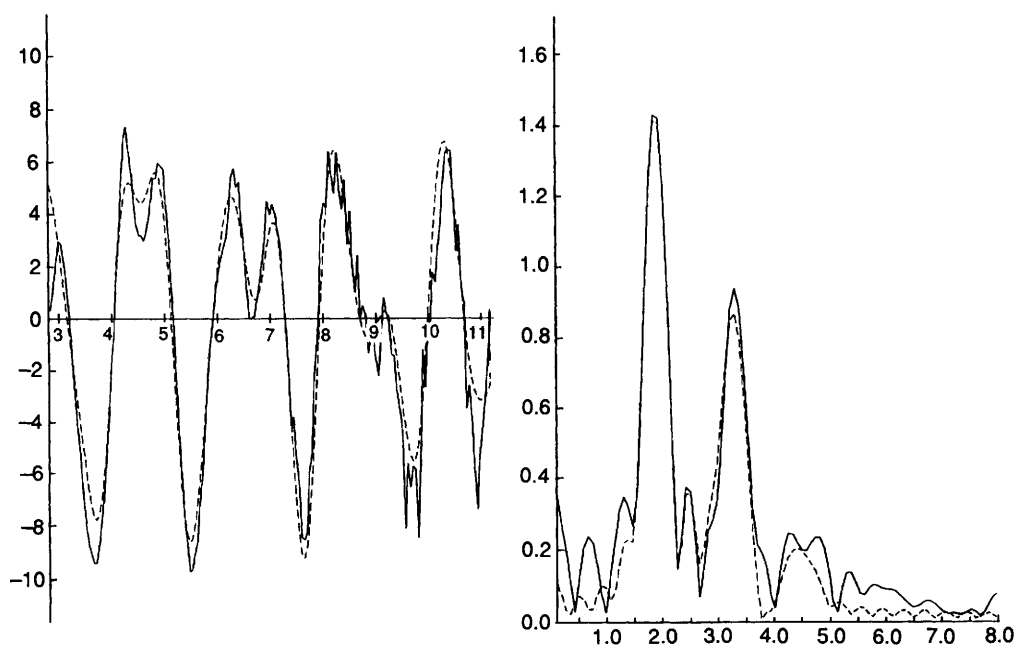


Fig. 3 The Zn K-edge k^3 -weighted EXAFS and Fourier transform, phase-shift corrected for oxygen, of $\text{Cu}(\text{acac})_2/\text{ZnEt}_2/\text{buta-1,3-diene}$ in DMF (10 mmol dm^{-3} Zn; 1:1: excess Zn:Cu:C₄H₆) at room temp. (—) Experiment and (---) spherical wave theory.

solution have been made.¹² When small metal particles are investigated by EXAFS, the apparent average coordination number is smaller than that observed in the bulk metal because of the high proportion of surface atoms; this effect is seen quite clearly in the Cu–Zn solutions. An additional effect arising from the substantial contribution of surface atoms is the apparent contraction of the metal–metal bonds in the particle compared to the bulk values, with deviations becoming more pronounced with decreasing particle size.¹³ Although small contractions in the 1st shell Cu–Cu distances in solution are observed when compared to bulk Cu (Table 1), the differences cannot be regarded as highly significant since they lie within the estimated precision limits of the XAS measurements.† Using the relationship between particle size and mean coordination number, derived for regular *fcc* copper crystals¹⁴ (Fig. 2), it is possible to estimate mean particle sizes of 500–600 atoms (*ca.* 25 Å length) and 80–100 atoms (*ca.* 12 Å length) for the Cu present in Cu(acac)₂/ZnEt₂/DMF and Cu(acac)₂/ZnEt₂/benzene solutions respectively. Treatment of Cu(acac)₂ with buta-1,3=diene prior to the addition of ZnEt₂ does not result in the formation of molecular copper species.

Addition of buta-1,3-diene does however appear to affect the coordination sphere of the Zn. The Zn K-edge EXAFS of Cu(acac)₂/ZnEt₂/DMF is best modelled by 2–3 oxygens at 1.96 Å, *ca.* one zinc at 3.11 Å and two shells of carbon atoms at 2.90 and 3.90 Å (Table 1). The EXAFS-derived coordination is not consistent with Zn(acac)₂ being the predominant species [the XANES also differs substantially from that of Zn(acac)₂] and can not be accommodated by the presence of unreacted ZnEt₂. EtZn(acac), reported to exist as a dissociating dimer (*n* = 1.6) in benzene at concentrations comparable to those used in the XAS experiments,¹⁵ would however be more consistent with the observed coordination. In contrast, the Zn K-edge EXAFS of the butadiene solution reveals an intense peak around 3–3.5 Å attributable to four zinc atoms (Fig 3, Table 1), suggesting the formation of a Zn–O cluster species. Such behaviour is not unusual for zinc complexes with simple oxygen-containing molecules as ligands. Methylzinc methoxide for example is known to be tetrameric with a cubic structure, and the structure of [Zn(OMe)₂·(EtZnOMe)₆] **1** is based on a double cube:¹⁶ the Zn K-edge EXAFS of a solution of **1**, prepared by the 1:1 addition of MeOH to ZnEt₂ in dry heptane, reveals a similarly intense peak around 3–3.5 Å due to backscattering from non-bonded Zn atoms (Table 1). It is therefore reasonable to suggest that a species derived from a single or double cube of zinc and oxygen atoms exists in the Cu/Zn/butadiene solution, although it is also likely that equilibria between several zinc species exist. Similar behaviour was noted for the Cu/Zn/benzene solutions.

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† X-Ray absorption spectra were recorded on Station 9.2 of the Synchrotron Radiation Source at the Daresbury Laboratory using a Si(220) order-sorting monochromator. Samples were prepared at room temp. in a nitrogen glove box and sealed in air-tight Al cells with Mylar windows. Owing to the low concentrations of Cu and Zn in the samples, spectra were acquired in fluorescence mode using a Canberra 13 element solid state detector and averaged (*ca.* 6 spectra per sample). Data reduction was performed using the programme PAXAS,⁵ and spherical wave curve fitting analyses, by least-squares refinement of non-Fourier filtered *k*³-weighted EXAFS, was executed in EXCURVE.⁶ Model compounds with known coordination sphere bond lengths were used to establish the transferability of phaseshift parameters. The accuracy of bonded and non-bonded interatomic distances is considered to be 1.4 and 1.6% respectively.⁷ Precisions on 1st shell coordination numbers are estimated to be *ca.* 5–10% and between 10–20% for non-bonded shells. The statistical validity of shells was assessed by published means⁸ and the numbers of independent parameters used in the fits fall within the guideline, $N_{\text{pts}} = 2(k_{\text{max}} - k_{\text{min}})(R_{\text{max}} - R_{\text{min}})\pi$ (ref. 9), unless otherwise stated. The *R*-factor is defined as $(\int |\chi^{\text{T}} - \chi^{\text{E}}| k^3 dk / \int |\chi^{\text{E}}| k^3 dk) \times 100\%$.

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