In situ sulfur K-edge X-ray absorption spectroscopy of the reaction of zinc oxide with hydrogen sulfide

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***In situ* sulfur K-edge XAS shows that the reaction of ZnO and H_2S proceeds *via* island formation of ZnS.**

Zinc oxide is employed as an absorbent to remove H_2S from petrochemical feedstocks and natural gas streams. Many transition-metal catalysts are poisoned by sulfur compounds. ZnO has a strong affinity for hydrogen sulfide [eqn. (1)], according to a reaction which has been known for many years.[1]

$$ZnO + H_2S \rightarrow ZnS + H_2O \qquad (1)$$

With an increasing need to purify gases this reaction is of significant importance industrially, indeed the use of a high surface area derivative of zinc oxide[2] is now routine in the petrochemical industry.[3–5] There remains however a significant absence of structural information about the process and little is known about the intermediate stages involved.

Extended X-ray absorption fine structure spectroscopy (EXAFS) and X-ray absorption spectroscopy (XAS) in the soft X-ray region (<5000 eV) is routine for static unchanging systems. However *in situ* studies at the sulfur edge have not been reported, almost certainly due to the high X-ray absorption coefficients in most gases at energies below 5000 eV. We report here the first results using sulfur XAS, *in situ*, to study reaction (1).

A small variable-temperature environmental cell was used to monitor *in situ* chemistry at soft X-ray edges. A powdered sample may be loaded into the central portion of the cell which is then sealed, evacuated and a pulse of gas admitted. Principle features of this cell include a large window[†] to accommodate a diffuse beam; a cylindrical design to minimise sample-to-detector distance and finally an ability to vary the angle of incident X-rays onto the sample to attain linearity of fluorescence yield. The cell is located within a He filled chamber (600 mbar).

Fig. 1 shows a stack plot of near-edge spectra recorded for 430 min following the addition of H_2S (1 bar) to dehydrated ZnO (1.5 g, 350 °C, 6 h at 10^{-5} Torr) at 50 °C. All data were recorded on beamline 3.4 at S.R.S.[‡] Daresbury Laboratory with fluorescence detection using a gas proportional counter. All spectra were referenced to sulfur (S_8) with a K-edge energy of 2472 eV.

Qualitative data analysis is possible by comparison with near-edge spectra of known compounds; at t = 40–80 min an intense feature is seen at 2478 eV following the white line at 2472 eV. No other oscillations were seen at higher energy and the near-edge structure shows little similarity with any standards. At t = 130 min after the addition the edge feature at 2473 eV has increased in intensity with a corresponding decrease in the feature at 2478 eV. The near-edge structure at this stage is very similar to H_2S gas; interestingly, however, the features are all considerably broadened in comparison to the gas phase spectra, suggesting possible surface chemisorption of H_2S or HS^-. By t = 430 min there is no trace of a feature at 2478 eV and oscillations have developed at higher energies past the edge. The near-edge structure is identical to that of ZnS. The absence

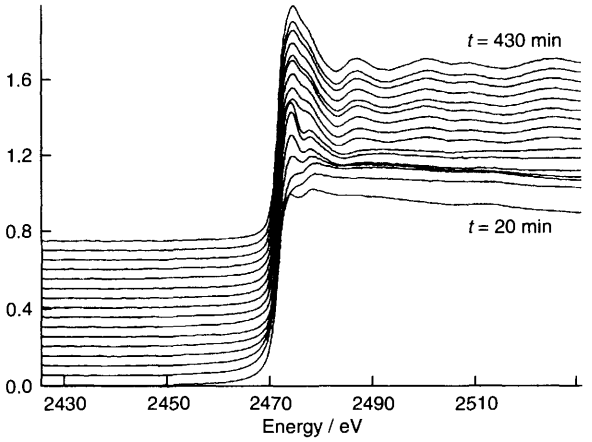

Fig. 1 A stack plot of S K-edge spectra following the addition of H_2S to ZnO at 50 °C. Initial and final spectra are marked (intermediate spectra were taken at the following times after the addition of H_2S: 40, 80, 100, 130, 150, 170, 230, 250, 270, 290, 310, 330, 360, 400 and 430 min respectively).

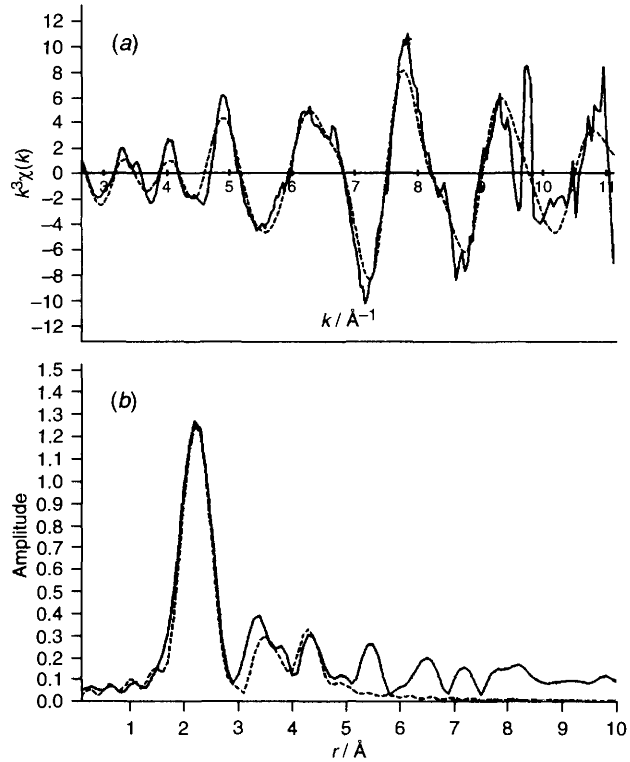

Fig. 2 (*a*) S K-edge k^3 weighted EXAFS and (*b*) Fourier transform, phase-shift corrected for zinc, of *ex situ* H_2S treated ZnO [ICI Katalco absorbent 32-4); (—) experimental, (---) spherical wave theory]

Table 1 EXAFS derived structural parameters for ZnO (ICI Katalco 32-4) absorbents. Statistical errors given in parentheses, global errors in distance determination have been estimated as 1.5%[6] and for coordination numbers 10–30%[7]

Zn K-edge: ZnO (ICI 32-4) H_2S treated $R^a = 36.5$; $F^b = 7.0$; $E_F{}^c = -6.58$;				S K-edge ZnO (ICI 32-4) H_2S treated $R^a = 38.2$; $F^b = 11.8$; $E_F{}^c = -6.19$;			
Atom	CN	r/Å	$2\sigma^2$/Å^2	Atom	CN	r/Å	$2\sigma^2$/Å
O	1.8(1)	1.960(6)	0.013(1)	—	—	—	—
S	2.0(1)	2.318(2)	0.010(1)	Zn	4.0(5)	2.304(3)	0.017(1)
Zn	5.6(3)	3.225(4)	0.021(1)	S	7.5(6)	3.768(13)	0.024(3)
O	4.5(5)	3.777(5)	0.011(1)	Zn	5.4(9)	4.410(11)	0.022(2)
S	2.6(5)	4.379(8)	0.0014(2)	—	—	—	—

$^a R = \int[\chi^T - \chi^E]k^3\,dk/\int\chi^E k^3\,dk \times 100$. $^b F = \Sigma_i\{[\chi^T - \chi^E]k_i{}^3\}^2$. $^c E_F$ = Fermi energy.

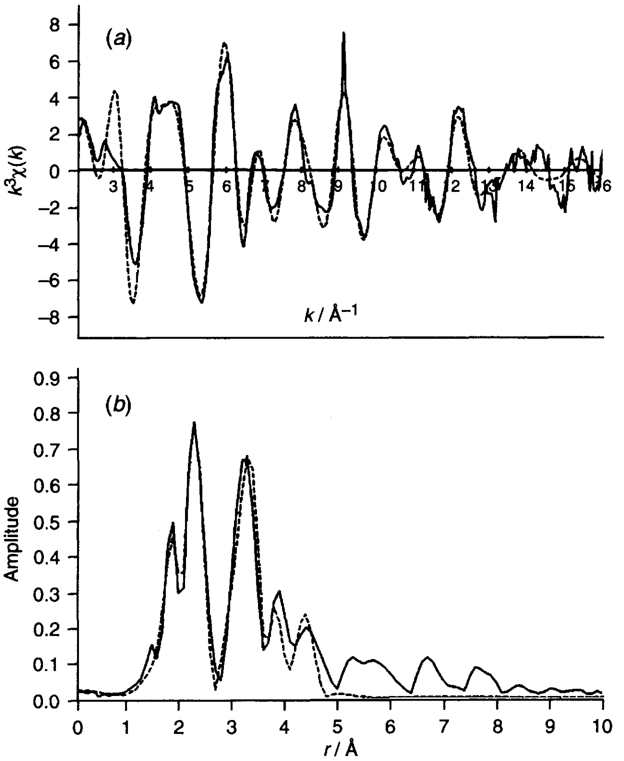

Fig. 3 (*a*) Zn K-edge k^3 weighted EXAFS and (*b*) Fourier transform, phase-shift corrected for sulfur, of *ex situ* H_2S treated ZnO (ICI Katalco 32-4) [(—) experimental, (---) spherical wave theory]

of any intense features at 2485 eV (characteristic for sulfates, sulfites *etc.*) suggests that formation of an oxysulfur intermediate is unlikely.

The final state S K-edge§ and Zn K-edge¶ EXAFS of a commercially available ZnO derivative‖ have also been collected after the ZnO has been treated, *ex situ* with H_2S.** Figs. 2 and 3 show the EXAFS and corresponding Fourier transform for the S and Zn K-edges respectively. EXAFS derived structural parameters are depicted in Table 1.

Analysis of the sulfur edge EXAFS (Table 1) shows good agreement between the ZnO absorbent and standard ZnS (blende) (ZnS: 4 Zn at 2.29 Å, 12 S at 3.75 Å, 12 Zn at 4.42 Å). Significantly, coordination numbers of the non-bonded shells are significantly reduced compared to ZnS (blende). This suggests only short-range order exists in the absorbents.

Analysis of the zinc edge data (Table 1) shows some similarity to ZnO itself (ZnO: 4 O at 1.96 Å, 12 Zn at 3.21 Å, 9 O at 3.75 Å). Additional shells are also seen in the Fourier transform which can successfully be modelled to sulfur at 2.32 and 4.38 Å. These results are consistent with the sulfur K-edge data and the distances are in close agreement with ZnS (blende) (ZnS: 4 S at 2.33 Å, 12 S at 4.44 Å). Again there is a significant reduction in coordination numbers for the non-bonded shells.

In summary we can conclude the following points about the interaction of H_2S and zinc oxide. First, as there is no apparent shift in the edge energies of the S K-edge spectra, there can be no change in oxidation state of the sulfur which remains as S^{-II} throughout the process. Secondly, as expected, sulfur coordinates directly to zinc and not oxygen in the initial stages of the process. Thirdly, EXAFS analysis of the final state of the reactants reveals a ZnS like phase which coexists with ZnO (wurtzite). All the data are consistent with a mechanism of formation involving islands of ZnS on the oxide surface. As the reaction proceeds these islands eventually form bulk regions of ZnS.

We would like to thank ICI Chemicals and Polymers and the University of Southampton for support and the head of the Daresbury Laboratory for the use of the S. R. S. facilities.

Footnotes

† 13 μm Kapton, dimensions 15 × 15 mm.

‡ S. R. S. operating in multibunch mode, 2 GeV, current 181–132 mA.

§ S. R. S. operating in multibunch mode, 2 GeV, current 257 mA, data recorded on station 3.4 in fluorescence mode using an InSb(111) monochromator; spectra referenced to sulfur (S_8).

¶ S. R. S. operating in multibunch mode, 2 GeV, current 187 mA, data recorded on station 7.1 in transmission mode using an Si(111) double-crystal monochromator; referenced to Zn metal foil at 9658 eV.

‖ High surface area ZnO, ICI Katalco 32-4 absorbent.

** ZnO 32-4 sulfided at ICI Billingham by 5% H_2S–CH_4 at 370 °C.

References

1 P. R. Westmoreland and D. P. Harrison, *Environ. Sci. Technol.*, 1976, **10**, 659; P. R. Westmoreland, J. B. Gibson and D. P. Harrison, *Environ. Sci. Technol.*, 1977, **11**, 488.
2 P. J. H. Carnell and P. E. Starkey, *Chem. Eng.*, 1984, **408**, 30.
3 P. J. H. Carnell, *Catalyst Handbook*, 2nd edn., ed. M. V. Twigg, Wolfe Publishing Ltd, London, 1989, ch. 4, pp. 196–220.
4 K. Eddington and P. Carnell, *Oil Gas J.*, 1991, **89**, 69.
5 G. W. Spicer and C. Woodward, *Oil Gas J.*, 1991, **89**, 76.
6 J. M. Corker, J. Evans, H. Leach and W. Levason, *J. Chem. Soc., Chem. Commun.*, 1989, 181.
7 B. K. Teo, *EXAFS: Basic Principles and Data Analysis*, Springer-Verlag, Berlin, 1986; S. J. Gurman, in *Applications of Synchrotron Radiation*, ed. C. R. A. Catlow and G. N. Greaves, Blackie, Glasgow, 1989.

Received, 16th February 1996; Com. 6/01160H