Infrared Study of Coadsorption of H_2S and CO_2 on γ-Alumina

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Summary Infrared results provide spectroscopic evidence that H_2S and CO_2 interact on γ-alumina giving rise to thiocarbonate surface species leading to the formation of carbonyl sulphide.

γ-Alumina is the most common catalyst in commercial use for the Claus reaction, equation (1). An i.r. study of

$$2\,H_2S + SO_2 \rightarrow 3\,S + 2\,H_2O \qquad (1)$$

sulphur dioxide adsorption on γ-alumina has been reported recently.[1] I.r. spectra of hydrogen sulphide chemisorbed on Al_2O_3 have been studied by Dalla Lana *et al.*[2,3] and by Slager and Amberg.[4] In particular two strong bands were observed at 1341 and 1568 cm^{-1}.[3,4] Slager and Amberg assigned the former to the $\delta(SH_2)$ mode of hydrogen bonded species and the latter to a ν(Al–O) vibration.[4] Recently, we noted that both bands were due to CO_2 traces admixed with H_2S.[5] As the wavenumbers are different from those given by CO_2 adsorbed on γ-Al_2O_3, we suspected that interaction between H_2S and CO_2 had taken place. We here report the results of i.r. studies of this surface interaction.

The γ-alumina used was from Degussa with a surface area of 90 $m^2\,g^{-1}$. The powder was pressed into the form of *ca.* 50 mg discs which were activated at 600 °C in a grease-free silica cell, and pretreated by heating in oxygen for 2 h followed by evacuation. The samples were then treated in 300 Torr of hydrogen for another 2 h followed by evacuation at the same temperature to a residual pressure of $< 10^{-5}$ Torr. This pretreatment removes adsorbed 'molecular' oxygen species which may transform H_2S into water.[3] I.r. spectra were recorded at room temperature with a Perkin-Elmer 580 grating instrument. Complementary gravimetric measurements were carried out in a conventional McBain thermobalance with 0·4 g samples of catalyst pretreated in the same way as before, the activation temperature being 500 °C. The adsorption pressure was kept very low (0·3—1·5 Torr). The chemisorbed amount is defined as the quantity remaining on alumina at 95 °C after cryogenic evacuation. 'Pure' H_2S or D_2S samples, without any trace of CO_2, were prepared from Al_2S_3 by hydrolysis with H_2O or D_2O.[6]

The admission of 'pure' H_2S to alumina causes a decrease in the intensity of the background OH band at 3785 cm^{-1} while bands at 2570 and 3680 cm^{-1} appear. No bands are detected in the 1700—1200 cm^{-1} range. Recently, Karge and Rasko,[7] studying H_2S adsorption on zeolites, showed that on aluminium-rich faujasites, H_2S molecules were adsorbed dissociatively. By analogy, we assign the 2570 and 3680 cm^{-1} bands to SH^- and OH groups formed from H_2S dissociative adsorption on alumina. Gravimetric measurements show that 80 $\mu mol\,g^{-1}$ of H_2S are chemisorbed on γ-Al_2O_3.

I.r. spectroscopic studies on the chemisorption of CO_2 on Al_2O_3 have already been carried out.[8,9] We find principal absorption bands at 3620, 1655, 1450, and 1228 cm^{-1} (Figure), due to various modes of vibration of HCO_3^- ions. According to Fink[10] and Knözinger,[9] these species are formed on Al-OH pair sites, called X-sites. Gravimetric measurements show that *ca.* 12 $\mu mol\,g^{-1}$ of CO_2 are strongly chemisorbed on γ-Al_2O_3 at 95 °C.

When H_2S is adsorbed on CO_2-treated γ-alumina, the HCO_3^- bands are weakened, while a new pair of bands appears at 1570 and 1340 cm^{-1} (Figure). Gravimetric measurements show that the number of H_2S molecules chemisorbed on γ-alumina is not sensitive to the preadsorption of CO_2. Adsorption of a mixture of H_2S and CO_2 (10:1) gives rise only to the pair of bands at 1570 and 1340 cm^{-1} in the 1700—1200 cm^{-1} range (Figure). Their wavenumber is not sensitive to substitution of D for H as the same bands occur on adsorbing a mixture of D_2S and CO_2. We assign them to carboxylate groups (ν_a and ν_s respectively) of species arising from interaction of H_2S (or D_2S) and CO_2 on the surface.

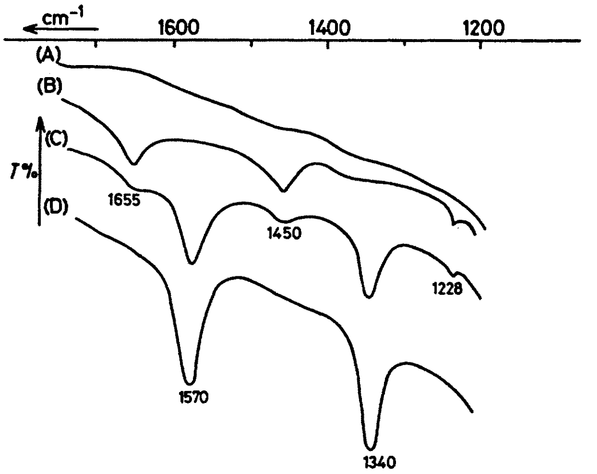
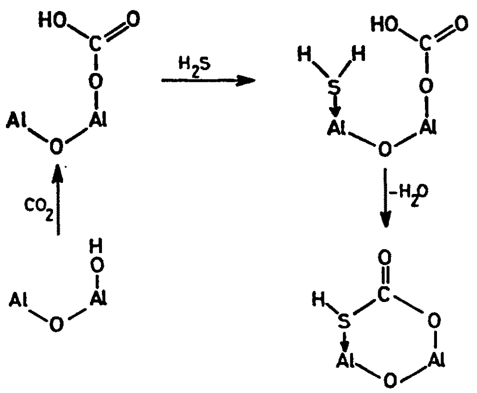


Figure. Spectra of CO_2 and H_2S on γ-alumina: (A) base line spectrum of activated disc; (B) CO_2 on Al_2O_3 after room temperature pumping; (C) (B) following exposure to H_2S (90 $\mu mol\ g^{-1}$); (D) coadsorption of H_2S and CO_2 (10:1) on alumina (100 $\mu mol\ g^{-1}$).

Coadsorption of H_2S and CO_2 on alumina leads to the formation of carbonyl sulphide: a band due to COS in the gas-phase surrounding the disc appears at 2060 cm^{-1}. Thus, we studied the adsorption of COS on γ-alumina. This adsorption gives no detectable changes in the intensities of i.r. bands due to surface hydroxy groups. New bands appearing at 1985 cm^{-1} (very weak) and 1945 cm^{-1} (weak) are due to chemisorbed COS. After a longer time of contact, the pair of bands at 1570 and 1340 cm^{-1} observed on coadsorption of H_2S and CO_2 on alumina becomes apparent. Bands due to HCO_3^- species also appear. These features are related to the formation of CO_2 from COS, which is confirmed by the chromatographic analysis of the gas-phase.

From the experimental data, we conclude that some H_2S molecules should be chemisorbed and activated at sites close to those leading to the formation of HCO_3^- species.



Scheme

This situation is allowed on the X-sites which have been described as acid–base pair sites consisting of a co-ordinatively unsaturated Al^{3+} ion and a basic OH group.[9,11] If we assume that hydrogen sulphide is held by co-ordination bonds on co-ordinatively unsaturated Al^{3+} ions, the surface interaction between H_2S and CO_2 on alumina may be visualized as in the Scheme.

The surface thiocarbonate species would be characterized by the pair of bands at 1570 and 1340 cm^{-1}. Their structure easily explains the formation of COS from H_2S and CO_2 on the surface. Similar species may be involved in the formation of CO_2 from COS on alumina. Haag and Miale[12] suggested almost similar surface thiocarbonate species to explain the formation of CO_2 from COS on MgO.

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