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## Infrared Study of Coadsorption of H<sub>2</sub>S and CO<sub>2</sub> on γ-Alumina

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Summary Infrared results provide spectroscopic evidence that  $H_2S$  and  $CO_2$  interact on  $\gamma$ -alumina giving rise to

thiocarbonate surface species leading to the formation of carbonyl sulphide.

 $\gamma$ -ALUMINA is the most common catalyst in commercial use for the Claus reaction, equation (1). An i.r. study of

$$2 \operatorname{H}_{2}S + SO_{2} \rightarrow 3 S + 2 \operatorname{H}_{2}O \tag{1}$$

sulphur dioxide adsorption on  $\gamma$ -alumina has been reported recently.<sup>1</sup> I.r. spectra of hydrogen sulphide chemisorbed on Al<sub>2</sub>O<sub>3</sub> have been studied by Dalla Lana *et al.*<sup>2,3</sup> and by Slager and Amberg.<sup>4</sup> In particular two strong bands were observed at 1341 and 1568 cm<sup>-1.3,4</sup> Slager and Amberg assigned the former to the  $\delta$ (SH<sub>2</sub>) mode of hydrogen bonded species and the latter to a v(Al-O) vibration.<sup>4</sup> Recently, we noted that both bands were due to CO<sub>2</sub> traces admixed with H<sub>2</sub>S.<sup>5</sup> As the wavenumbers are different from those given by CO<sub>2</sub> adsorbed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, we suspected that interaction between H<sub>2</sub>S and CO<sub>2</sub> had taken place. We here report the results of i.r. studies of this surface interaction.

The  $\gamma$ -alumina used was from Degussa with a surface area of  $90 \text{ m}^2 \text{ g}^{-1}$ . 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<sub>2</sub>S into water.<sup>3</sup> 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' H2S or D2S 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<sup>-1</sup> while bands at 2570 and 3680 cm<sup>-1</sup> appear. No bands are detected in the 1700—1200 cm<sup>-1</sup> range. Recently, Karge and Rasko,' 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<sup>-1</sup> bands to SH<sup>-</sup> and OH groups formed from  $H_2S$  dissociative adsorption on alumina. Gravimetric measurements show that 80  $\mu$ mol g<sup>-1</sup> of  $H_2S$  are chemisorbed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

I.r. spectroscopic studies on the chemisorption of CO<sub>2</sub> on Al<sub>2</sub>O<sub>3</sub> have already been carried out.<sup>8,9</sup> We find principal absorption bands at 3620, 1655, 1450, and 1228 cm<sup>-1</sup> (Figure), due to various modes of vibration of HCO<sub>3</sub><sup>-</sup> ions. According to Fink<sup>10</sup> and Knözinger,<sup>9</sup> these species are formed on Al-OH pair sites, called X-sites. Gravimetric measurements show that ca. 12 µmol g<sup>-1</sup> of CO<sub>2</sub> are strongly chemisorbed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 95 °C.

When  $H_2S$  is adsorbed on  $CO_2$ -treated  $\gamma$ -alumina, the  $HCO_3^-$  bands are weakened, while a new pair of bands appears at 1570 and 1340 cm<sup>-1</sup> (Figure). Gravimetric measurements show that the number of  $H_2S$  molecules chemisorbed on  $\gamma$ -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



FIGURE. Spectra of CO<sub>2</sub> and H<sub>2</sub>S on y-alumina: (A) base line spectrum of activated disc; (B) CO<sub>2</sub> on Al<sub>2</sub>O<sub>3</sub> after room temperature pumping; (C) (B) following exposure to H<sub>2</sub>S (90  $\mu$ mol g<sup>-1</sup>); (D) coadsorption of H<sub>2</sub>S and CO<sub>2</sub> (10:1) on alumina (100  $\mu$ mol g<sup>-1</sup>).

1340 cm<sup>-1</sup> in the 1700—1200 cm<sup>-1</sup> 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 ( $v_a$  and  $v_g$  respectively) of species arising from interaction of H<sub>2</sub>S (or  $D_2S$ ) and  $CO_2$  on the surface.

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<sup>-1</sup>. Thus, we studied the adsorption of COS on  $\gamma$ -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<sup>-1</sup> (very weak) and 1945 cm<sup>-1</sup> (weak) are due to chemisorbed COS. After a longer time of contact, the pair of bands at 1570 and 1340 cm<sup>-1</sup> 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  $HCO_{\overline{s}}$  species.



This situation is allowed on the X-sites which have been described as acid-base pair sites consisting of a co-ordinatively unsaturated Al<sup>3+</sup> ion and a basic OH group.<sup>9,11</sup> If we assume that hydrogen sulphide is held by co-ordination bonds on co-ordinatively unsaturated Al<sup>3+</sup> 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  $1340 \text{ cm}^{-1}$ . Their

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structure easily explains the formation of COS from H<sub>2</sub>S and CO<sub>2</sub> on the surface. Similar species may be involved

in the formation of CO<sub>2</sub> from COS on alumina. Haag and

Miale<sup>12</sup> suggested almost similar surface thiocarbonate

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