

Supported Metal Catalysts: Preparation, Characterisation, and Function

IV. Study of Hydrogen Sulphide and Carbonyl Sulphide Adsorption on Platinum Catalysts

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The adsorption of carbonyl sulphide and hydrogen sulphide onto a range of supported platinum catalysts has been studied. The interaction between carbon monoxide and the sulphur-containing compounds was investigated by (i) preadsorbing carbon monoxide then adsorbing hydrogen sulphide or carbonyl sulphide, (ii) preadsorbing hydrogen sulphide or carbonyl sulphide followed by carbon monoxide adsorption, and (iii) coadsorption of carbon monoxide and the sulphur-containing compound. Isotopically labelled carbon monoxide was used to study the exchange processes occurring between carbonyl sulphide and carbon monoxide. In general, preadsorption of hydrogen sulphide blocked all carbon monoxide adsorption. On Pt/silica catalyst preadsorption of carbon monoxide reduced hydrogen sulphide adsorption by 81%. Coadsorption resulted in enhanced carbon monoxide adsorption on Pt/alumina and Pt/silica. On Pt/molybdena(I) (prepared by impregnation) the adsorption of both compounds was decreased, while on Pt/molybdena(C) (prepared firing a cocrystallized precursor), which was better dispersed, the adsorption capacity was unchanged. Adsorption of carbonyl sulphide was principally nondissociative. However, adsorption studies involving labelled carbon monoxide did reveal that a minority of the adsorbed carbonyl sulphide was dissociated on Pt/silica and on Pt/alumina (6 and 15%, respectively). No dissociation was detected on Pt/molybdena(I) and Pt/molybdena(C). © 1996 Academic Press, Inc.

INTRODUCTION

Sulphur is defined as a nonspecific catalyst poison that can dramatically reduce catalytic activity (for a general review, see Refs. (1, 2)). At low concentrations, however, it has been used to modify catalytic properties. These effects are explained by making use of both electronic and geometric aspects of catalytic reactions on surfaces. For example, adsorbed sulphur will poison the site on which it is adsorbed, and it may also poison a larger number of sites by removing a geometrical degree of freedom from the surface (1, 2). In addition the formation of a bond between a metal atom in an array and a sulphur atom may affect the ability of neigh-

boring metal atoms to form bonds of the correct strength to allow a catalytic reaction to occur. This type of behavior has been well understood for many years, at least empirically, and has been used to good effect in the reforming industry (3). For example, sulphur addition in platinum-catalyzed reforming reduces the amount of carbon laydown and increases the rate of reaction (4). The effects of sulphur on catalyst selectivity are well documented in the area of carbon monoxide hydrogenation (5–7). In the case of carbon monoxide hydrogenation over Rh/silica, the addition of sulphur results in an eightfold increase in the selectivity to methanol (5). This change in product distribution and yield is believed to be due to an electronic effect of the sulphur on the strength of the C–O bond. With carbon monoxide hydrogenation over Ni/alumina (7), on the other hand, the authors of the study concluded that sulphur poisoned the ability of the surface to hydrogenate more severely than the ability to form carbon–carbon bonds. In propane dehydrogenation, the addition of sulphur to a Pt/alumina catalyst has been shown to decrease the propensity of the catalyst to produce methane in the non-steady-state period by blocking sites that catalyze hydrogenolysis (8).

The above summary gives an impression of the effects that can be achieved by having a poison such as sulphur adsorbed on a surface when a reaction is occurring. The effect of the sulphur is often determined by the nature and energetics of the adsorption site. To examine these properties it is now common for adsorption studies to be performed on well-characterized single-crystal surfaces. However, although the adsorption of hydrogen sulphide on platinum has been investigated both on single-crystal and supported systems (9–11), it has not had the extensive amount of research that has been undertaken on the sulphur on nickel system (1). When the system is further complicated the level of research decreases proportionally; e.g., the interaction between hydrogen sulphide and carbon monoxide has only had limited attention (12, 13). This lack of research is compounded when the adsorption of carbonyl sulphide and the interaction between carbonyl sulphide and carbon

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monoxide, are considered (14, 15). This dearth of coadsorption data has significant industrial implications as it is rare for an industrial system not to involve competitive adsorption. Therefore, as part of a larger study on adsorption and reaction of platinum catalysts, we undertook a limited study of sulphur adsorption with the aim of understanding the adsorption/coadsorption phenomena on well-characterized, supported-metal catalysts.

In this series of papers we have studied the preparation, characterization, and function of supported platinum catalysts (16–19). This has involved a thorough investigation using physical characterization techniques (16), as well as studies of carbon monoxide, dioxygen, and hydrocarbon adsorption (17, 18). In this article we have further extended the adsorption studies on these well-characterized, supported-catalyst systems to include hydrogen sulphide adsorption, carbonyl sulphide adsorption, and coadsorptions involving isotopically labelled carbon monoxide.

EXPERIMENTAL

Apparatus and Procedures

Chemisorption studies were performed in a dynamic mode using a pulse-flow microreactor system in which the catalyst sample was placed on a sintered glass disc in a vertical tube (8 mm i.d., down flow) inside a furnace. The reactant pulses were introduced into the gas stream immediately above the catalyst bed using a sample loop of identical dimensions to the reactor. Using this system the catalysts (typically 0.3–0.5 g) could be reduced *in situ* in flowing 5% dihydrogen in dinitrogen by heating to 573 K at 7 K min⁻¹. When reduction was complete the gas flow was changed to helium (60 cm³ min⁻¹) and the catalyst was held at 573 K until no dihydrogen could be detected in the effluent. The catalyst was cooled to 293 K under flowing helium and the adsorbate gas was admitted by injecting pulses of known size (typically 2.515 cm³, 6.67 × 10³ Pa) into the helium carrier-gas stream and hence on to the catalyst. In all cases the whole pulse was analysed by on-line GC-MS. The amount of gas adsorbed, from any pulse, was determined from the difference between a calibration peak area and the peak area obtained following the injection of pulses of comparable size onto the catalyst. The typical detection limit for adsorption is 2 × 10¹⁷ molecules g⁻¹. Desorptions were performed by heating the catalyst to 573 K in flowing helium. After thermal desorption the catalyst was cooled again in flowing helium. Adsorptions and desorptions were followed using a gas chromatograph fitted with a thermal conductivity detector and a Porapak Q column coupled to a mass spectrometer (Spectramass SM100D).

Chemisorptions were determined at ambient temperature and at pressures up to 2.67 × 10³ Pa by using [³⁵S]hydrogen sulphide in a static system. The system used was of similar design to that described elsewhere (19).

Materials

Both the helium (Air Products, 99.998%) and the 5% dihydrogen in dinitrogen (ICI) were further purified by passing through activated palladium bronze to remove any oxygen impurity and then through a bed of Carbosorb AS (BDH) to remove any water impurity. Hydrogen sulphide and carbonyl sulphide (both BDH) were further purified using a freeze/thaw technique. [¹⁸O]Carbon monoxide and [¹³C]carbon monoxide were supplied by Amersham International and were used without further purification. [³⁵S]Hydrogen sulphide (specific activity 0.132 mCi mmol⁻¹ and 0.196 mCi mmol⁻¹) was diluted with nonradioactive hydrogen sulphide to the required activity.

Catalyst Preparation

A full description of the preparation of the catalysts has been given elsewhere (16). In summary, three catalysts were prepared by impregnation of the supports by sufficient aqueous chloroplatinic acid solution to achieve a 1% w/w Pt loading on the silica and alumina and a 0.5% w/w Pt loading on the molybdenum trioxide. The loadings obtained were 0.76% w/w Pt/silica(I), 0.88% w/w Pt/alumina(I), and 0.49% w/w Pt/molybdenum trioxide(I). A fourth catalyst, 0.55% w/w Pt/MoO₃(C), was prepared by cocrystallization of PtCl₂ and ammonium molybdate, followed by firing at 723 K. Analysis of the catalysts by HRTEM and EXAFS (16) gave an order for the average particle size of Pt/MoO₃(C) < Pt/Al₂O₃ < Pt/SiO₂ ≪ Pt/MoO₃(I); however, apart from the Pt/MoO₃(I) sample, all the catalysts have high dispersions (approaching 100%). For example, the Pt/Al₂O₃ catalyst has over 60% of the Pt crystallites smaller than 7 Å and none above 40 Å, while the Pt/SiO₂ catalyst has over 55% below 7 Å and none above 62 Å.

RESULTS

Hydrogen Sulphide Adsorption

Aliquots of hydrogen sulphide were pulsed over freshly reduced samples at 10-min intervals. The amount adsorbed on each of the catalysts at 273 K is reported in Table 1. The amount adsorbed on the alumina and silica supports, which had been through a reduction procedure, was also determined. This procedure was not adopted for the molybdena support as without spillover hydrogen the support structure present in the catalyst will not be obtained (9). Once uptake had ceased the catalysts were heated to 573 K in flowing helium and the desorption noted (Table 2).

When [³⁵S]hydrogen sulphide was adsorbed on a sample of reduced Pt/silica (0.137 g) in a static system, a surface saturation count rate of 1550 counts min⁻¹ was obtained. When the system was evacuated for 0.5 h the surface count rate fell to 1478 counts min⁻¹, corresponding to a 4.6% decrease in surface activity. When 2.7 × 10³ Pa of nonradioactive hydrogen sulphide was left to equilibrate with the previously

TABLE 1
Hydrogen Sulphide and Carbonyl Sulphide Adsorption^a

Catalyst	Amount adsorbed ^b ($\times 10^{18}$)		
	H ₂ S	COS	CO ^c
Al ₂ O ₃	39.2	— ^d	—
Pt/Al ₂ O ₃	55.9 ± 2.0	9.1 ± 2.5	19.8 ± 1.1
Pt/MoO ₃ (C)	52.8 ± 0.4	47.3 ± 9.0	4.9 ± 0.8
Pt/MoO ₃ (I)	74.3 ± 1.6	69.7 ± 0.6	5.2 ± 0.8
Pt/SiO ₂	3.7 ± 2.6	2.5 ± 2.0	2.4 ± 0.5
SiO ₂	1.2	— ^d	—

^a Adsorption capacities measured at 273 K.

^b Units, molecules g⁻¹.

^c Data from Ref. (17).

^d Not measured.

evacuated surface for 3 h there was no further decrease in surface radioactivity.

Adsorption of [³⁵S]hydrogen sulphide on a sample of reduced Pt/alumina (0.196 g) in a static system resulted in a surface saturation count rate of 4150 counts min⁻¹. Evacuation of the system for 0.5 h resulted in a decrease in surface count rate of 96 counts min⁻¹, corresponding to a decrease in surface activity of 2.3%. Nonradioactive hydrogen sulphide (2.7 × 10³ Pa) was admitted to the system to equilibrate with the previously evacuated surface for 3 h, after which time a final surface count rate of 3746 counts min⁻¹ was recorded: this corresponds to a further decrease of 7.6% or an overall decrease from the initial value of 9.7%.

Carbonyl Sulphide Adsorption

Pulses of carbonyl sulphide were passed over each of the catalysts, immediately after reduction, at 12-min intervals. The amount adsorbed on each of the catalysts at 273 K is detailed in Table 1. Once uptake had ceased the catalysts were heated to 573 K in flowing helium and the desorption was noted (Table 3).

Carbon Monoxide Adsorption on a Hydrogen Sulphide Precovered Surface

After reduction each catalyst was saturated with hydrogen sulphide at 273 K. Once uptake of the hydrogen sul-

TABLE 2
Thermal Desorption of H₂S

Catalyst	Desorption peak maximum (K)	Evolved gas	Amount of gas evolved ($\times 10^{18}$) ^a
Pt/MoO ₃ (C)	403	H ₂ S	53.5
	503	H ₂ S	Trace
Pt/MoO ₃ (I)	418	H ₂ S	54.1
Pt/SiO ₂	—	—	0.0

^a Units, molecules g⁻¹.

TABLE 3
Thermal Desorption of COS

Catalyst	Desorption peak maximum (K)	Evolved gas	Amount of gas evolved ($\times 10^{18}$) ^b
Pt/MoO ₃ (C)	523	CO	
	368	COS	3.5
Pt/MoO ₃ (I)	398	CO	4.6
	373	COS	11.5
Pt/SiO ₂	543	CO ₂	13.9
	—	—	0.0

^a Evolution observed by mass spectrometry, no measurable peaks detected by GC.

^b Units, molecules g⁻¹.

phide had ceased aliquots of carbon monoxide were passed over the catalysts and the amount adsorbed determined (Table 4). Carbon monoxide was only adsorbed on the alumina-supported sample. After adsorption, the catalysts were heated to 573 K in flowing helium and the desorption was followed (Table 4).

Hydrogen Sulphide Adsorption on a Carbon Monoxide Precovered Surface

Carbon monoxide was adsorbed to saturation on each of the catalysts after reduction. Immediately after saturation with carbon monoxide, aliquots of hydrogen sulphide were passed over the catalysts. The results are detailed in Table 5. Displacement of 0.70 × 10¹⁸ molecules g⁻¹ of carbon monoxide was observed when the initial pulse of hydrogen sulphide was passed over the Pt/alumina catalyst. When the first pulse of hydrogen sulphide was passed over the Pt/MoO₃(I) catalyst, 3.11 × 10¹⁸ molecules g⁻¹ of carbon monoxide were desorbed. When all adsorption of hydrogen sulphide had ceased the catalyst was heated to 573 K in the carrier gas stream and the desorption products were monitored by GC-MS. The results for each catalyst are shown in Table 5.

TABLE 4
Adsorption and Desorption of CO on an H₂S Precovered Surface^a

Catalyst	Amount of H ₂ S preadsorbed ^b	Amount of CO adsorbed ^b	Thermal desorption		
			Gas evolved	Amount ($\times 10^{18}$) ^b	Temp. (K)
Pt/Al ₂ O ₃	57.3	0.4	H ₂ S	3.0	368
			CO	^c	503
Pt/MoO ₃ (C)	53.1	0.0	H ₂ S	6.4	353
Pt/MoO ₃ (I)	73.8	0.0	H ₂ S	7.4	373
Pt/SiO ₂	1.8	0.0	—	0.0	—

^a Adsorption capacities measured at 273 K.

^b Units, molecules g⁻¹ ($\times 10^{18}$).

^c Trace amount detected by mass spectrometry.

TABLE 5

Adsorption and Desorption of H₂S on a CO Precovered Surface^a

Catalyst	Amount of CO preadsorbed ^a	Amount of H ₂ S adsorbed ^b	Thermal desorption		
			Gas evolved	Amount ($\times 10^{18}$) ^b	Temp. (K)
Pt/Al ₂ O ₃	19.7	56.2	H ₂ S	^c	363
			CO	^c	383
			CO	^d	498
			CO	^d	548
Pt/MoO ₃ (C)	4.7	44.4	H ₂ S	12.6	353
Pt/MoO ₃ (I)	3.6	76.0	H ₂ S	7.3	363
Pt/SiO ₂	2.9	0.7	—	0.0	—

^a Adsorption capacities measured at 273 K.^b Units, molecules g⁻¹ ($\times 10^{18}$).^c Coincidence of the GC peaks for the two gases prevented quantification.^d Trace quantities detected by mass spectrometry.*Coadsorption of Carbon Monoxide and Hydrogen Sulphide*

A 1 : 1 mixture of hydrogen sulphide and carbon monoxide was passed over each of the catalysts and the adsorption of each component ascertained. The results are shown in Table 6. After adsorption the catalysts were heated to 573 K in flowing helium and the desorption was noted (Table 6).

Carbon Monoxide Adsorption on a Carbonyl Sulphide Precovered Surface

Pulses of carbonyl sulphide were passed over each of the reduced catalysts until uptake ceased. Once the catalysts were saturated with carbonyl sulphide, pulses of iso-

TABLE 6

Co-Adsorption and Subsequent Desorption of a 1 : 1 CO : H₂S Mixture^a

Catalyst	Amount adsorbed ^b ($\times 10^{18}$)		Thermal desorption		
	H ₂ S	CO	Gas evolved	Amount ($\times 10^{18}$) ^b	Temp. (K)
Pt/Al ₂ O ₃	50.4	23.4	H ₂ S	^c	363
			CO	^c	383
			CO	^d	503
			CO ₂	^d	563
Pt/MoO ₃ (C)	43.3	4.8	H ₂ S	17.5	403
			H ₂ S	Trace	503
Pt/MoO ₃ (I)	58.8	3.0	H ₂ S	12.2	413
Pt/SiO ₂	0.8	4.0	CO	0.8	433
			CO	3.3	523

^a Adsorption capacities measured at 273 K.^b Units, molecules g⁻¹ ($\times 10^{18}$).^c Coincidence of the GC peaks for the two gases prevented quantification.^d Trace quantities detected by mass spectrometry.

TABLE 7

Adsorption and Desorption of CO on a COS Precovered Surface^a

Catalyst	Amount of COS preadsorbed	Amount of CO adsorbed ^b	Thermal desorption		
			Gas evolved	Amount ($\times 10^{18}$) ^b	Temp. (K)
Pt/Al ₂ O ₃	10.9	2.1	CO	^c	423
			CO ₂	^c	573
			CO	^d	353
Pt/MoO ₃ (C)	46.8	4.1	CO	^d	353
			COS	^d	368
			CO ₂	^d	388
Pt/MoO ₃ (I)	70.1	4.1	CO	Trace	363
			COS	10.7	373
			CO ₂	20.6	388
Pt/SiO ₂	4.5	1.3	—	0.0	—

^a Adsorption capacities measured at 273 K.^b Units, molecules g⁻¹ ($\times 10^{18}$).^c Detected by mass spectrometry.^d Coincidence of the GC peaks for the gases prevented quantification.

topically labelled carbon monoxide (¹²C¹⁸O : ¹³C¹⁶O = 1 : 1) were passed over the samples. The adsorption results are given in Table 7. With all the samples the carbon monoxide retained its chemical integrity, but with the Pt/alumina and Pt/silica catalysts the isotopically labelled carbon monoxide exchanged with the CO component of the preadsorbed carbonyl sulphide. The amount of exchange was 1.6×10^{18} molecules g⁻¹ with Pt/alumina; i.e., 15% of the adsorbed COS can exchange, whilst with Pt/silica 0.26×10^{18} molecules g⁻¹ (6% of the adsorbed COS) can exchange. The catalysts were heated to 573 K in flowing helium after all adsorption had ceased. Carbon monoxide was desorbed from the Pt/MoO₃(I) catalyst and showed no evidence of isotope exchange; carbon dioxide was also desorbed from this catalyst and mass spectral analysis showed it to be solely ¹²C¹⁶O₂.

Carbonyl Sulphide Adsorption on a Carbon Monoxide Precovered Surface

After reduction each catalyst was saturated with isotopically labelled carbon monoxide (¹²C¹⁸O : ¹³C¹⁶O = 1 : 1); when no further carbon monoxide could be adsorbed, pulses of carbonyl sulphide were passed over the catalysts. The adsorption results are reported in Table 8. No exchange between the preadsorbed carbon monoxide and the carbonyl sulphide was detected. However, 0.45×10^{18} molecules g⁻¹ of carbon monoxide were desorbed when the first pulse of carbonyl sulphide was passed over the Pt/MoO₃(I) catalyst. When no further adsorption was observed the catalysts were heated to 573 K in the carrier gas and the desorption was monitored (Table 8). During thermal desorption over the Pt/silica catalyst peaks at *m/z* 44 and 45 were detected but no higher *m/z* fragments were observed.

TABLE 8

Adsorption and Desorption of COS on a CO Precovered Surface^a

Catalyst	Amount of COS preadsorbed	Amount of COS adsorbed ^b	Thermal desorption		
			Gas evolved	Amount ($\times 10^{18}$) ^b	Temp. (K)
Pt/Al ₂ O ₃	22.2	0.0	CO ₂	10.2	573
Pt/MoO ₃ (C)	5.8	35.3	COS	4.1	373
			CO ₂	6.0	413
			CO	Trace	363
Pt/MoO ₃	1.7	36.6	COS	11.4	373
			CO ₂	4.8	388
Pt/SiO ₂	6.6	0.0	—	0.0	—

^a Adsorption capacities measured at 273 K.

^b Units, molecules g⁻¹ ($\times 10^{18}$).

DISCUSSION

Hydrogen Sulphide Adsorption/Desorption

The adsorption of hydrogen sulphide on these catalysts shows up both similarities and differences. One of the major differences observed between the molybdena-supported catalysts on the one hand and the alumina- and silica-supported catalysts on the other was the significant interaction between the sulphur and the reduced molybdena support (16). Indeed with the Pt/MoO₃(I) sample the amount of sulphur adsorbed is equivalent to the formation of a surface layer of MoS₂. This was not unexpected as the interaction between sulphur and molybdena has been well documented in studies involving hydrodesulphurization over alumina-supported cobalt- and nickel-molybdena catalysts (20). On thermal desorption, however, the Pt/MoO₃(C) catalyst desorbed all hydrogen sulphide, whereas with Pt/MoO₃(I) only 73% desorbed. For desorption of hydrogen sulphide to occur the hydrogen atoms must be retained by the system. Therefore adsorption of hydrogen sulphide on the molybdenum bronze derived from reduction of the Pt/MoO₃(C) catalyst cannot result in formation of a molybdenum sulphide and desorption of water. The same is true for 73% of the adsorbed hydrogen sulphide on the Pt/MoO₃(I) catalyst; however, the remaining 27% may indeed react to give a surface sulphide with concomitant desorption of water.

The results obtained from adsorption of radioactively labelled hydrogen sulphide indicate that there are two types of adsorbed hydrogen sulphide, distinguishable by their strength of adsorption, and three different adsorption sites: (i) a site which bonds sulphur strongly and will not exchange; (ii) a site which binds sulphur weakly and is removable under vacuum; and (iii) a site which will allow exchange between gas and adsorbed phases when a pressure of the gas is present. All three sites were present on Pt/alumina (91, 2, and 7%, respectively) while only two were present on Pt/silica (95, 5, and 0%, respectively). The Pt/MoO₃ samples

were not examined. The detection of a weakly and strongly bound species agrees with the literature concerning hydrogen sulphide adsorption at high temperatures (21, 22). The results also agree with those of Paál and co-workers (11) who found, using radioactively labelled hydrogen sulphide, that very little of the sulphur was removed by evacuation.

With Pt/silica, once the support adsorption has been discounted, comparable adsorption capacities were obtained between carbon monoxide and hydrogen sulphide. We have shown in an earlier study (17) that 90% of the carbon monoxide adsorption on Pt/silica is linearly bound and, therefore, the Pt_s:S ratio must be equally close to 1:1. Similar ratios have been found in other studies (1, 23) when high concentrations of hydrogen sulphide have been used. This adsorbed sulphur species, detected in the pulse experiments, can be directly related to the strongly bound species, which did not exchange, that is observed in the radiochemical adsorption experiments.

The amount of hydrogen sulphide adsorbed on Pt/alumina gives a S:Pt ratio of 2.1:1, which, if all the sulphur is associated with the platinum, would give a stoichiometric compound PtS₂. However, it has been documented (24) that hydrogen sulphide will adsorb on the acid sites of alumina, typically between 39 and 107 $\mu\text{mol g}^{-1}$, and indeed a significant amount of hydrogen sulphide was adsorbed on the support (approximately 65 $\mu\text{mol g}^{-1}$) in the absence of the platinum (Table 1). If the amount adsorbed on the support is subtracted from the total adsorption, a figure of 16.7×10^{18} molecules of hydrogen sulphide is obtained for adsorption on the metal. This gives an S:Pt ratio of 0.6:1 which is in good agreement with the 0.7:1 ratio obtained from carbon monoxide adsorption. Ponitzsch *et al.* (11) obtained a S:CO ratio of 1.84:1 for adsorption on a Pt/alumina catalyst without correction for adsorption on the support. This is in good agreement with our data before correction. In their study (11), although they were aware of adsorption on the support, no account of this was taken when calculating the S:CO ratio. A value of 0.6:1 was also found by Apesteguía *et al.* (21) for total sulphur adsorption on the metallic function of a Pt/Al₂O₃-Cl catalyst. However, it should be remembered that the S:Pt ratio has been found to be sensitive to surface topography (2) with values below 0.5 for Pt(111) and as high as 0.8 on Pt(110).

Interaction of Carbon Monoxide and Hydrogen Sulphide

Pt/silica. The results of the interaction of carbon monoxide and hydrogen sulphide with Pt/silica can be summarized as follows: (i) when hydrogen sulphide was preadsorbed on Pt/silica no subsequent carbon monoxide adsorption was detected, (ii) when carbon monoxide was preadsorbed the amount of hydrogen sulphide adsorbed decreased by 81%, and (iii) when carbon monoxide and hydrogen sulphide were cofed, the amount of hydrogen sulphide adsorbed decreased by 78% while the amount of

carbon monoxide adsorbed increased by 67% (Table 1, cf. Table 6). The absence of carbon monoxide adsorption on a sulphur precovered surface was expected and indeed has been reported previously (25); however, one must be careful in interpreting the lack of carbon monoxide adsorption when hydrogen sulphide is preadsorbed. As the adsorption of hydrogen sulphide is dissociative (26), then there may be no mechanism by which the sulphur can desorb and hence no sites can be liberated for carbon monoxide adsorption. Indeed, this interpretation is supported by the results obtained from the carbon monoxide preadsorption and from the coadsorption study. These indicate that on ca. 80% of the surface sites carbon monoxide is more strongly adsorbed than hydrogen sulphide. The remaining 20%, on which carbon monoxide does not adsorb, but which can adsorb hydrogen sulphide, represents hydrogen sulphide adsorption on the silica support. The enhancement of carbon monoxide adsorption when cofed with hydrogen sulphide is interesting and may be interpreted as follows. In a previous paper on carbon monoxide adsorption (17) we showed that the adsorption of carbon monoxide was deleteriously affected by residual hydrogen left from the reduction procedure. It was also shown that when dioxygen adsorption removed this residual hydrogen, enhanced adsorption could be obtained (17). When the carbon monoxide and hydrogen sulphide are coadsorbed the hydrogen sulphide will adsorb and be displaced by carbon monoxide; however, hydrogen sulphide can cause desorption of some component of this hydrogen (8), possibly by a surface reconstruction, and hence an enhanced carbon monoxide adsorption would be expected.

Pt/alumina. The results for the interaction between carbon monoxide and hydrogen sulphide on Pt/alumina can be summarized as follows: (i) when hydrogen sulphide was preadsorbed, subsequent carbon monoxide adsorption was reduced to 2% of the amount of carbon monoxide which could be adsorbed on a fresh surface, (ii) when carbon monoxide is preadsorbed there was no reduction in adsorptive capacity for hydrogen sulphide, and (iii) when carbon monoxide and hydrogen sulphide were cofed, hydrogen sulphide adsorption was reduced by 10% while carbon monoxide adsorption was enhanced by 18%. In contrast to the silica result, a small quantity of carbon monoxide can adsorb on a hydrogen sulphide precovered Pt/alumina and, as there was no coincident displacement of hydrogen sulphide, sites are available on which carbon monoxide, but not hydrogen sulphide, can adsorb. However, differences in the behavior of the catalysts cannot be assumed on the strength of this result, as 2% of the amount of carbon monoxide adsorbed on the Pt/silica system is within the limits of detection.

When hydrogen sulphide was passed over a carbon monoxide precovered surface, 4% of the adsorbed carbon monoxide was displaced, indicating that hydrogen sulphide

can adsorb on the metal function in the presence of carbon monoxide. The adsorption of hydrogen sulphide on to the alumina in the presence of preadsorbed carbon monoxide was expected (accounting for approximately 70% of the hydrogen sulphide adsorption). However, the absence of any reduction in the adsorptive capacity for hydrogen sulphide indicates that carbon monoxide does not block hydrogen sulphide adsorption on the metal sites. The effect of the hydrogen sulphide adsorption is seen in the desorption behavior of the carbon monoxide. In the absence of hydrogen sulphide, carbon dioxide is a significant desorption product (44% of the adsorbed carbon monoxide is desorbed as carbon dioxide (17)), whereas when hydrogen sulphide has been adsorbed only a trace quantity of carbon dioxide can be detected. Such behavior has been observed previously with platinum catalysts (12, 27). In cases (27–29) where the carbon dioxide is formed from a Boudouard reaction, the effect of the sulphur on the carbon monoxide has been interpreted as principally electronic, with the electronegative sulphur withdrawing electron density from the antibonding orbitals of the adsorbed carbon monoxide and hence strengthening the C≡O bond. In the current system, however, it has been shown that the carbon dioxide was produced from the reaction of adsorbed carbon monoxide with the hydroxyl groups from the alumina support (17).

When the gases are coadsorbed, it would appear from the loss in hydrogen sulphide adsorption (5.5×10^{18} molecules g^{-1}) and gain in carbon monoxide adsorption (3.6×10^{18} molecules g^{-1}) that, under these conditions, carbon monoxide can adsorb on a portion of the sites which are used by hydrogen sulphide when it adsorbs on a carbon monoxide precovered surface (approximately 10%). Even with this increase in adsorptive capacity the CO: Pt ratio remains below 1:1.

Pt/molybdena(I). The interaction between hydrogen sulphide and carbon monoxide on Pt/MoO₃(I) can be summarised as follows: (i) preadsorption of hydrogen sulphide blocks all subsequent carbon monoxide adsorption; (ii) when carbon monoxide was preadsorbed there was no reduction in hydrogen sulphide adsorptive capacity; (iii) on coadsorption, hydrogen sulphide adsorption decreased by 20% while carbon monoxide adsorption decreased by 42%. However, while there was no detectable carbon monoxide adsorption on the hydrogen sulphide preadsorbed surface, the desorption of the preadsorbed hydrogen sulphide was modified such that less material was desorbed and the temperature at which the rate of desorption reached a maximum was reduced by ca. 50 K. Therefore, a nonadsorbed gas has affected the surface energetics of an adsorbed gas. Such behavior has been observed in various other studies (27, 30), but previously has not been satisfactorily interpreted. Recently, however, single-crystal studies on the transfer of energy from gas-phase molecules to adsorbed species through translational interactions (31) and the modification

of the adsorbed state by collisions with inert gases (32) does allow at least a qualitative interpretation of the phenomena. It is interesting also that the effect is only significantly seen with the catalyst that has the largest platinum crystallites, mirroring the single-crystal studies, but suggesting that the smaller crystallites are not susceptible to this phenomenon.

When hydrogen sulphide was passed over a carbon monoxide precovered surface, 86% of the carbon monoxide adsorbed was displaced, indicating that hydrogen sulphide can adsorb on the metal function in the presence of carbon monoxide. The adsorption of hydrogen sulphide on to the molybdena support in the presence of preadsorbed carbon monoxide, which is adsorbed solely on the metal function, was expected. The absence of any reduction in the adsorptive capacity for hydrogen sulphide may indicate that the remaining carbon monoxide does not block hydrogen sulphide adsorption on the metal sites but the amount of carbon monoxide remaining is so small relative to the hydrogen sulphide adsorption that any effect may be within experimental error.

The coadsorption results again indicate that hydrogen sulphide adsorption is unaffected by the presence of carbon monoxide, whereas there is a loss in carbon monoxide adsorptive capacity, as would be expected from the preadsorption results.

Pt/molybdena(C). For Pt/MoO₃(C) the interaction between carbon monoxide and hydrogen sulphide can be summarised as follows: (i) when hydrogen sulphide was preadsorbed there was no subsequent adsorption of carbon monoxide, (ii) when carbon monoxide was preadsorbed there was no reduction in hydrogen sulphide adsorption capacity; (iii) when carbon monoxide and hydrogen sulphide were coadsorbed the adsorption capacities were unaffected. These results indicate that in general, hydrogen sulphide and carbon monoxide adsorb on separate sites and do not interfere; the exception is when hydrogen sulphide is preadsorbed. This conclusion is not too unexpected since hydrogen sulphide preadsorption results in a significant loss of carbon monoxide adsorption capacity and since the vast majority of the hydrogen sulphide adsorptive capacity of the catalysts is not on the metal but on the support.

Carbonyl Sulphide Adsorption/Desorption

When carbonyl sulphide was adsorbed on fresh catalysts there was no evidence of the dissociative chemisorption from liberation of carbon monoxide as that observed with nickel catalysts (14). Rather the adsorption behavior was similar to that observed on rhodium catalysts (15). The adsorption capacities for carbonyl sulphide were considerably less than those measured for hydrogen sulphide which is in keeping with the behavior found on rhodium catalysts (15). The results also indicated that there was no adsorption of the carbonyl sulphide on the alumina support whereas when hydrogen sulphide was the adsorbate there was consider-

able adsorption on the alumina support. Thermal desorption from Pt/alumina only gave rise to carbon monoxide with desorption maxima similar to those obtained from carbon monoxide/hydrogen sulphide coadsorption. This suggests that carbonyl sulphide dissociation occurred on adsorption with both fragments, S and CO, being retained at 293 K.

With the molybdena samples it appeared that carbonyl sulphide adsorption occurred on the support as well as on the metal. As there was no carbon monoxide, or carbon dioxide, liberated during the adsorption, the adsorption of carbonyl sulphide on the molybdena supports was molecular. This was confirmed by the thermal desorption, which showed that the low-temperature desorption peak was carbonyl sulphide. Only at higher temperatures did the adsorbed carbonyl sulphide undergo dissociation with resultant desorption of carbon monoxide/dioxide.

Interaction of Carbon Monoxide and Carbonyl Sulphide

Pt/silica. When carbon monoxide was preadsorbed there was no subsequent adsorption of carbonyl sulphide. It is likely that this lack of adsorption is due to the absence of ensembles large enough to accommodate the carbonyl sulphide when carbon monoxide is already present on the surface. The lack of adsorption can be viewed as a site-blocking phenomenon rather than carbon monoxide necessarily being the more strongly bound species. Indeed, the results of the carbon monoxide adsorption on a carbonyl sulphide precovered surface indicate that carbonyl sulphide is the stronger adsorber.

The amount of carbon monoxide adsorbed on a carbonyl sulphide precovered surface was reduced from that of a clean surface by 46%. As no carbonyl sulphide was desorbed it can be assumed that the carbon monoxide adsorption takes place on vacant sites (ensembles) which are insufficient, either in terms of geometrical size or electronic configuration, for carbonyl sulphide adsorption but can facilitate carbon monoxide. When this experiment was performed using isotopically labelled carbon monoxide, it was found that exchange processes occurred such that 6% of the CO from the preadsorbed carbonyl sulphide can exchange with gas-phase carbon monoxide. This supports the view that a proportion of the carbonyl sulphide does dissociate on adsorption but with no carbon monoxide desorption.

Pt/alumina. No adsorption of carbonyl sulphide was observed on a carbon monoxide-covered surface and the thermal desorption profile was typical of carbon monoxide in the absence of any sulphur compounds.

Carbon monoxide adsorption on a carbonyl sulphide preadsorbed surface was reduced by 89% indicating a more efficient blocking of carbon monoxide adsorption than that observed with the Pt/silica. Examination of the amount of exchange observed when the adsorbate carbon monoxide was isotopically labelled showed that 15% of the adsorbed

carbonyl sulphide had a CO component that was able to exchange with gas-phase carbon monoxide. If this does indeed represent the portion of the adsorbed carbonyl sulphide that has dissociated, then the increased amount of dissociation, in comparison with the Pt/silica, may explain the greater loss in carbon monoxide adsorption capacity with the Pt/alumina.

Pt/molybdena(I). When carbonyl sulphide was pulsed over Pt/molybdena saturated with carbon monoxide, 11% of the adsorbed carbon monoxide was desorbed by the first carbonyl sulphide pulse. No further displacement of carbon monoxide was observed. The amount of carbonyl sulphide adsorbed decreased from that obtained with a clean sample by 47%. Comparing these results with those obtained from Pt/silica and Pt/alumina it appears that the carbon monoxide adsorption on the metal component of the Pt/molybdena(I) has a lower density and hence allows a sufficient ensemble size to be present for carbonyl sulphide adsorption. Note that if the preadsorbed carbon monoxide is isotopically labelled there is no exchange between it and the carbonyl sulphide.

Carbon monoxide adsorbed on a carbonyl sulphide precovered surface, but no exchange processes were observed, suggesting that there was no dissociation of the carbonyl sulphide or that the amount was below the detection limits. The adsorptive capacity for carbon monoxide was decreased by 17% from that of a fresh sample, which is a considerably smaller reduction than that observed with the Pt/alumina or Pt/silica. The reason for this is not clear but a possible mechanism would be that the adsorption of carbon monoxide can liberate sufficient energy to facilitate spillover of the carbonyl sulphide from the metal to the molybdena support.

Pt/molybdena(C). Carbonyl sulphide adsorbed on a carbon monoxide precovered surface but the amount was reduced by 25% compared with that on a clean surface. However, in contrast to the result from Pt/molybdena(I), there was no concomitant displacement of the preadsorbed carbon monoxide. This suggests that all the measured carbonyl sulphide adsorption was on the molybdena and not on the platinum.

On a carbonyl sulphide-covered surface, carbon monoxide adsorbed and again there was no exchange. In this case the amount adsorbed, although lower than that obtained with a fresh sample, was within the error limits of the measurement and hence we cannot be definitive about the extent of reduction in adsorptive capacity.

CONCLUSIONS

The adsorption of carbonyl sulphide and hydrogen sulphide onto a series of well-characterised supported platinum catalysts has been studied. The interaction between CO and the sulphur-containing compounds was investi-

gated by (i) preadsorbing CO then adsorbing H₂S or COS, (ii) preadsorbing H₂S or COS followed by CO adsorption, and (iii) coadsorption of CO and the sulphur-containing compound. Isotopically labelled CO was used to study the exchange processes occurring between COS and CO. In general, the results from the adsorption of H₂S on the catalysts were supportive of the data from the literature. However, on the Pt/Al₂O₃ catalyst a site which allowed exchange between gas and surface but was stable under dynamic pumping was identified. This type of behavior, which has been observed for carbon monoxide adsorption (17), has not been observed previously for hydrogen sulphide. We have shown that the Pt/Al₂O₃ catalyst has a narrow particle size distribution and strong metal-support interaction which imparts δ^+ character to the metal (16). Whether it is a surface topographical effect, an electronic effect, or a combination of both that gives rise to this site we are unsure at present. On all the catalysts preadsorption of hydrogen sulphide blocked all carbon monoxide adsorption. However, with the Pt/MoO₃(I) catalyst an effect of the nonadsorbed carbon monoxide was seen on the desorption of the hydrogen sulphide. This phenomenon appears to be related to particle size in that only the catalyst with the largest particle size showed the effect. Coadsorption resulted in enhanced carbon monoxide adsorption on Pt/alumina and Pt/silica, whereas on Pt/molybdena(I) the adsorption of both compounds was decreased, while on the Pt/molybdena(C) the adsorption capacity was unchanged.

Adsorption of COS was principally nondissociative. Adsorption studies involving labelled CO, however, did reveal that a small fraction of the adsorbed COS was dissociated on the Pt/silica and on the Pt/alumina (6 and 15% respectively). No dissociation was detected on either of the Pt/molybdena catalysts.

It is interesting that the most reactive catalysts were the Pt/Al₂O₃ and the Pt/SiO₂, which have similar particle sizes that lie between those found for the two molybdena-supported catalysts, while the Pt/MoO₃(I) catalyst with the largest particle size showed effects that were in agreement with single-crystal studies. In general, therefore, we can ascribe most of the phenomena observed to surface topography linked to particle size rather than to a direct support effect (as distinct from the support influencing the particle size) or the δ^+ character of the metal (no evidence was found for any δ^+ character with the Pt/SiO₂ catalyst (16)).

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