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Carbonyl Sulphide Adsorption on Supported Rhodium

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The adsorption and thermal desorption of carbonyl sulphide on rhodium/silica have been studied. Three distinct forms of adsorbed carbonyl sulphide have been detected, at 293 K, using isotopically labeled carbon monoxide as a probe molecule. Thermal desorption resulted in dissociation of all adsorbed carbonyl sulphide and the subsequent desorption of carbon monoxide; no carbonyl sulphide was desorbed.

INTRODUCTION

The adsorption of carbonyl sulphide on rhodium has not been studied previously; indeed, carbonyl sulphide adsorption in general has been investigated only on a few metals (*1*), and hence there is little in the literature on the modes of adsorption. The most recent study of carbonyl sulphide adsorption on nickel (*2*) indicated total dissociative adsorption even at 193 K and we were interested to know whether there was similar behaviour when carbonyl sulphide was adsorbed on rhodium.

METHODS AND MATERIALS

The apparatus used throughout this study was an all-glass pulse-flow microreactor system. Using this system, the samples could be activated in flowing hydrogen, maintained in flowing helium, and then covered by adsorbate gas by injecting pulses of known size into the helium carrier-gas stream and hence to the sample. 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 sample. Adsorptions and desorptions were followed using a TCD gas chromatograph, fitted with a Porapak Q-S column, coupled to a mass spectrometer (Spectramass SM100D fitted with a high resolution RF head).

Two adsorbents were used in this study, rhodium trichloride/silica and rhodium oxide/silica. The rhodium trichloride silica was prepared by adding silica (Davison 952, surface area 259 $m^2\ g^{-1}$) to an aqueous solution of the compound and evaporating to dryness. The rhodium oxide/silica was prepared by heating rhodium nitrate/silica (prepared as per rhodium trichloride) to 723 K in flowing air (>100 $cm^3\ min^{-1}$) for a period of 2 h. After the supported salt was dried, 0.50 g was placed in the reactor on a glass sinter and reduced in a flow of hydrogen (80 $cm^3\ min^{-1}$) by heating to 573 K. The sample was cooled in flowing hydrogen and maintained in a flow of helium (80 $cm^3\ min^{-1}$). Pulses of carbonyl sulphide (0.2 cm^3, 1.01×10^5 Pa) or carbon monoxide (2.95 cm^3, 6.67×10^3–2.00×10^4 Pa) were passed over the adsorbent at 293 K until adsorption was complete; the sample was then heated in flowing helium to 573 K at 25 K min^{-1} and the effluent gas was passed through a trap at 78 K.

Noncondensed gases were continuously monitored by GC-MS. After desorption had ceased the trap was warmed to 323 K and the contents analysed. The catalyst was then cooled in flowing helium and the adsorption–desorption cycle repeated. Both

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TABLE 1

Carbonyl Sulphide Adsorption

Sample	%Rh (w/w)	Amount COS ads. (μmol g^{-1})	COS/Rh	Amount CO ads. (μmol g^{-1})	CO/Rh
Rh(Cl)/SiO_2	1.2	32.6	0.3	131.7	1.1
Rh(O)/SiO_2	1.7	18.3	0.1	51.1	0.3

the helium (BOC, 99.998%) and the hydrogen (BOC, 99.9998%) were further purified by passing through an activated palladium bronze to remove any oxygen impurity and through a bed of soda asbestos to remove any water impurity. Carbonyl sulphide (BDH, 97%) was further purified by freezing and pumping. All isotopically labeled gases were supplied by Amersham International and were used as received.

RESULTS

Pulses of carbonyl sulphide, at 13-min intervals, were passed over the samples immediately after reduction. The amount of carbonyl sulphide adsorbed on the fresh surface is shown in Table 1; the amount of carbon monoxide adsorbed is also shown for comparison. During the adsorptions small amounts of gas were evolved, 0.7 μmol g^{-1} of carbon dioxide from the rhodium (trichloride)/silica and 0.2 μmol g^{-1} of carbon monoxide from the rhodium oxide-derived sample. When adsorption ceased the samples were heated to 573 K in flowing helium; the noncondensable gas, which passed through a trap at 78 K, was continuously monitored by GC-MS and was confirmed as carbon monoxide. The carbon monoxide desorption profiles, from the carbonyl sulphide adsorption, are shown in Fig. 1 along with desorption profiles obtained from carbon monoxide adsorption. The amount desorbed was equal to the amount of carbonyl sulphide adsorbed, i.e., no CO units, whether as CO or COS, were retained by the samples after thermal desorption. On warming the trap no carbonyl sulphide was detected.

The process of adsorption/thermal desorption was repeated until two successive adsorptions gave similar results. The adsorptive capacity decreased to steady-state values of 2.1 μmol g^{-1} for Rh(Cl)/silica (*cf.* a steady-state value with respect to carbon monoxide of 33.4 μmol g^{-1}) and 0.5 μmol g^{-1} for Rh(O)/silica (*cf.* 20.9 μmol g^{-1} for carbon monoxide). To investigate the mode of carbonyl sulphide adsorption, carbon monoxide was used as a probe. Isotopically labeled carbon monoxide ([^{13}C]CO and [^{18}O]CO) was pulsed over a steady-state surface saturated with carbonyl sulphide and the isotopic profile of that part of the pulse which did not adsorb was measured.

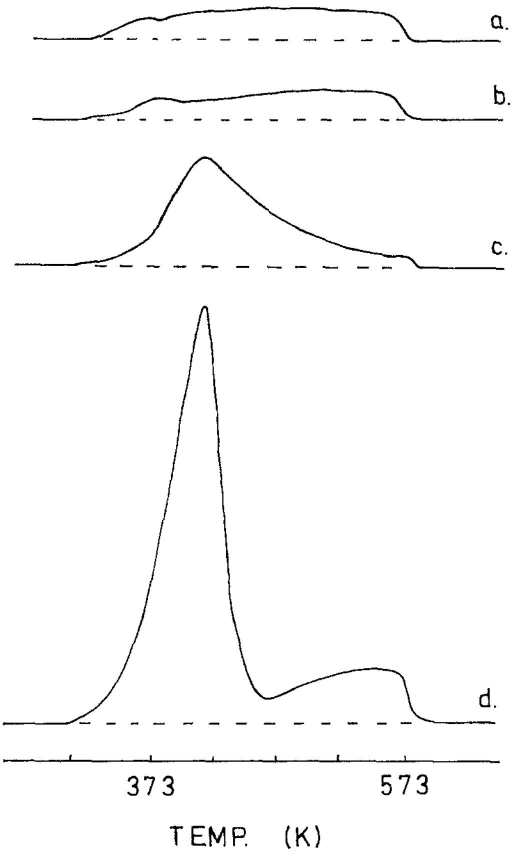

Fig. 1. Thermal desorption profiles of carbon monoxide (a) after COS adsorption over Rh(O)/SiO_2, (b) after CO adsorption over Rh(O)/SiO_2, (c) after COS adsorption over Rh(Cl)/SiO_2, and (d) after CO adsorption over Rh(Cl)/SiO_2.

TABLE 2

Adsorption of CO on a COS-Precovered Surface

Sample[a]	Amount of COS preads. (μmol)	CO adsorption					
		PN[b]	Amount			Exit ratio	
			Pulse	Ads.	Exit	12:13	18:16
Rh(Cl)/SiO$_2$	1.1	1	15.1	9.8	5.3	1.4:1	1.0:1
		2	15.0	3.0	12.0	1.2:1	1.2:1
		3	14.9	0.0	14.9	1.1:1	1.4:1
		Ref.	14.8	—	14.8	1.1:1	1.4:1
		Total ads.		12.8			
Rh(O)/SiO$_2$	0.3	1	14.9	3.9	11.0	1.2:1	1.3:1
		2	14.8	1.1	13.7	1.1:1	1.4:1
		3	14.7	0.8	13.9	1.1:1	1.4:1
		4	14.6	0.0	14.6	1.1:1	1.4:1
		Ref.	14.5	—	14.5	1.1:1	1.4:1
		Total ads.		5.0			

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[a] Weight of samples, 0.5 g.

[b] PN, pulse number.

TABLE 3

COS Adsorption on CO-Precovered Rh(Cl)/SiO$_2$[a]

Amount CO preads. (μmol)	Ratio of preads. CO		COS adsorption					
	12:13	18:16	PN[b]	Amount			Ratio in disp. gas	
				Pulse	Ads.	Disp.	12:13	18:16
16.7	1.0:1	1.2:1	1	8.3	0.6	0.7CO	1.0:1	0.9:1
			2	8.3	0.4	0.6CO	1.0:1	1.0:1
			3	8.3	0.0	0.0	—	—
			Total ads.		1.0			

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[a] Weight of sample, 0.5 g.

[b] PN, pulse number.

The results are shown in Table 2. Clearly there has been exchange between the CO unit of the carbonyl sulphide and the gas-phase CO, giving an increase in the [^{12}C, ^{16}O]CO component of the exit gas. Combining the GC and MS analysis it is possible to quantify the extra amount of [^{12}C, ^{16}O]CO in the exit gas. The amount of carbon exchange, with the chloride-derived sample, was 52% relative to the amount of carbonyl sulphide adsorbed; however, the amount of oxygen exchanged was 83%. With the oxide-derived sample the amount of carbon and oxygen exchanged was the same at 87% relative to the amount of carbonyl sulphide adsorbed. The reverse procedure was also used to investigate the carbonyl sulphide mode of adsorption. Carbonyl sulphide was pulsed over samples which were in the steady state with respect to carbon monoxide adsorption and were already saturated with isotopically labeled carbon monoxide. The results for the catalyst derived from rhodium trichloride are shown in Table 3. The amount of oxygen, preadsorbed as carbon monoxide, which can be exchanged is 0.5%; no exchange was observed between the carbon atoms. On the rhodium (oxide)/silica however there was no carbonyl sulphide adsorption or carbon monoxide displacement. Both samples were then heated to 573 K and cooled to 293 K, and carbonyl sulphide was adsorbed; as soon as the surface was saturated with carbonyl sulphide, pulses of labeled carbon monoxide were passed over the samples. The results are shown in Table 4. Again by combining the GC and MS results the degree of exchange has been determined; with the Rh(Cl)/silica sample 26% of the carbon and 35% of the oxygen preadsorbed as carbonyl sulphide was exchanged, while with the Rh(O)/silica sam-

TABLE 4

CO Adsorption on a COS-Precovered Surface on Samples Which Were in the Steady State with Respect to CO Adsorption

Sample[a]	Amount of COS preads. (μmol)	CO adsorption					
		PN[b]	Amount			Exit ratio	
			Pulse	Ads.	Exit	12:13	18:16
Rh(Cl)/SiO$_2$	7.9	1	15.9	4.9	11.0	1.3:1	0.6:1
		2	15.9	1.6	14.3	1.2:1	0.8:1
		3	15.8	0.0	15.8	0.9:1	1.1:1
		Ref.	15.7	—	15.7	0.9:1	1.1:1
		Total ads.		6.5			
Rh(O)/SiO$_2$	4.7	1	16.5	2.8	13.7	1.7:1	0.7:1
		2	16.4	9.8	6.6	1.3:1	1.0:1
		3	16.4	1.0	15.4	1.1:1	1.3:1
		4	16.3	0.0	16.3	1.2:1	1.4:1
		Ref.	16.2	—	16.2	1.2:1	1.4:1
		Total ads.		13.6			

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[a] Weight of samples, 0.5 g.

[b] PN, pulse number.

ple 28% of the carbon and 62% of the oxygen preadsorbed as carbonyl sulphide was exchanged.

DISCUSSION

This discussion will be principally concerned with the mode of carbonyl sulphide adsorption and the reactivity of the adsorbed species.

From Table 1 it is clear that adsorbed carbonyl sulphide requires a more extensive site than carbon monoxide; indeed, if each carbon monoxide occupies a single site, then the site requirement of the carbonyl sulphide is greater than two. The evolution of carbon monoxide and carbon dioxide during the adsorption indicates that there is some (~1–2%) dissociative adsorption. This is significantly different from that observed for carbonyl sulphide adsorption over nickel films, where at 293 K there was considerable evolution of carbon monoxide (*2*). However, the lack of such evolution does not imply that the adsorption is associative; the carbonyl sulphide may dissociate on contact with the surface only for the carbon monoxide to be adsorbed on a suitable vacant site.

On thermal desorption no carbonyl sulphide is desorbed, but only carbon monoxide, and therefore there is dissociation prior to desorption. For this to occur it is likely that the adsorbed carbonyl sulphide is adsorbed "lying down" with the OCS axis parallel to the surface or bent with the CS axis parallel to, but the oxygen pointing away from, the surface. The desorption profiles (Fig. 1) obtained from desorption of carbon monoxide and carbonyl sulphide are similar but not identical. This is not surprising as the presence of sulphur on the surface from whatever source would be expected to alter the desorption characteristics of carbon monoxide (*3–5*). However, the desorption profiles do suggest that the carbonyl sulphide is dissociated, as it would be expected that decomposition of carbonyl sulphide to give gas-phase carbon monoxide and adsorbed sulphur would give rise to a sharp desorption/decomposition peak rather than a shape similar to that for adsorbed carbon monoxide.

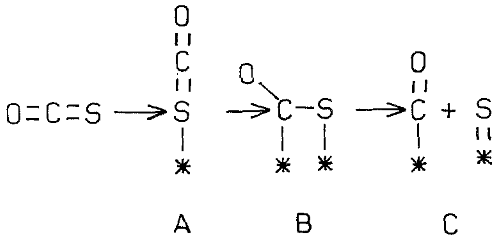
When the adsorbents were saturated with carbonyl sulphide it was found that there was still a considerable number of free sites as detected by carbon monoxide chemisorption. Approximately 20% of the initial CO adsorption (25.5 μmol g^{-1} for Rh(Cl)/silica and 11.6 μmol g^{-1} for Rh(O)/silica) was adsorbed on carbonyl sulphide-saturated surfaces, again reinforcing the view that the site requirement for carbonyl sulphide is more stringent than that for carbon monoxide. When the same experiment is repeated with isotopically labeled carbon monoxide with a pulse-by-pulse analysis (Table 2) exchange is observed between the adsorbed carbonyl sulphide and the carbon monoxide. With Rh(O)/silica the amount of carbon and oxygen exchange was 87% relative to the amount of carbonyl sulphide adsorbed. This type of exchange between adsorbed and gas-phase species has been observed previously over rhodium with carbon monoxide (*6*). Therefore if a similar mechanism operates at least 87% of the adsorbed carbonyl sulphide is dissociated to CO(ads) + S(ads). In the case of Rh(Cl)/silica the behaviour is slightly more complex in that there is a difference between the amount of carbon and the amount of oxygen exchanged; 83% of the oxygen adsorbed as carbonyl sulphide is exchangeable but only 52% of the carbon. Therefore 52% of the adsorbed carbonyl sulphide dissociates to CO(ads) + S(ads) and exchanges as outlined above.

However, of the remaining 48% of adsorbed carbonyl sulphide, 65% must be in a state which allows oxygen exchange but not carbon exchange. There are at least three ways in which this may take place: (i) the carbonyl sulphide may dissociate to give O(ads) + CS(ads); (ii) the carbonyl sulphide may dissociate to give CO(ads) + S(ads) followed by a concerted reaction between labeled and nonlabeled carbon monoxide, i.e.,

$$[^{18}O]CO(g) + CO(a) \rightarrow CO(g) + [^{18}O]CO(a),$$

$$[^{13}C]CO(g) + CO(a) \rightarrow [^{13}C]CO(g) + CO(a);$$

or (iii) a concerted reaction between labeled carbon monoxide and nondissociated carbonyl sulphide may occur. Various studies have shown that on pulsing carbon monoxide over a rhodium surface which contains adsorbed oxygen, carbon dioxide is formed (*3, 7–9*). No carbon dioxide was detected, therefore implying that dissociation of carbonyl sulphide to give O(a) + CS(a) does not occur. If isotopically labeled carbon monoxide is pulsed over a surface containing carbon monoxide, then it has been shown that there will be exchange; however, there is no evidence for scrambling (*6*). Similarly in this system no evidence was found for scrambling when the isotopically labeled carbon monoxide was pulsed over the carbonyl sulphide-covered surface. Therefore as adsorbed carbon monoxide retains its molecular integrity a concerted mechanism to allow oxygen transfer cannot be occurring. Hence mechanism (ii) above may be discounted. By default this leaves mechanism (iii), but this is not sufficient to justify its correctness. For mechanism (iii) to be significantly different from mechanism (ii) there is a requirement that in some way the sulphur weakens the C–O bond and hence makes the oxygen susceptible to exchange. This is not unreasonable as the C—O bond strength in OCS is less than that in CO. Therefore if the carbonyl sulphide is adsorbed such that both the carbon and the sulphur are bonded to the surface, then a weakening of the C–O bond will occur as long as the C–S bond is maintained (Scheme 1). Such a species may be considered an intermediate to full dissociation of carbonyl sulphide (the asterisks in Scheme 1 represent adsorption sites as distinct from rhodium atoms). It is required that the oxygen exchange process is concerted as otherwise there is the likelihood of carbon dioxide formation. The mechanism may be similar to that found with carbon monoxide exchange on copper catalysts (*10*), where again no carbon dioxide was formed.



Scheme 1.

Therefore from the exchange data we may put approximate figures on the ratio of species (A), which does not exchange either carbon or oxygen, species (B), which will allow oxygen exchange but not carbon, and species (C), which will allow both carbon and oxygen exchange. The oxide-derived sample gives an (A) : (B) : (C) ratio of 1 : 0 : 6.7, while the chloride-derived sample gives an (A) : (B) : (C) ratio of 1 : 1.8 : 3.1. Therefore on Rh(O)/silica sample there is a large proportion of full dissociation. The difference between the samples, in terms of their ability to adsorb/dissociate carbonyl sulphide, can be explained by the differences in their dispersion. The Rh(oxide)/silica has a lower dispersion (as measured by carbon monoxide chemisorption) and hence a larger particle size. As the bonding requirements of carbonyl sulphide prior to dissociation should be more easily accommodated by a larger particle than by a small one, i.e., small particles favour single-site bonding whereas larger particles favour multi-site bonding, then the oxide-derived sample should exhibit a higher degree of dissociation.

When carbonyl sulphide was pulsed over rhodium (oxide)/silica which had been saturated with carbon monoxide there was no adsorption or displacement. As carbonyl sulphide has a more stringent site requirement than carbon monoxide, it is probable that there is no site available for adsorption and hence no possible displacement. However, when a similar experiment was performed using the rhodium (trichloride)/silica there was adsorption of carbonyl sulphide and displacement of carbon monoxide. When the preadsorbed carbon monoxide was isotopically labeled, 8.5% of the oxygen adsorbed as carbonyl sulphide was detected in the displaced carbon monoxide (Table 3) but no carbon exchange was detected. Given that in the reverse situation there was 83% exchange of the carbonyl sulphide oxygen it is clear that the ratio of adsorbed states of carbonyl sulphide has altered, i.e., the ratio (A) : (B) : (C) has changed from 1 : 1.8 : 3.1 to 10.8 : 1 : 0. Even allowing for such changes in adsorbed state it is surprising that on a surface saturated with carbon monoxide there are still sites available for carbonyl sulphide adsorption. Clearly there is only a small number of such sites but the total amount adsorbed (2.0 μmol g^{-1}) is almost equal to the steady-state value of 2.1 μmol g^{-1} obtained for carbonyl sulphide adsorption. Therefore there are a limited number of carbonyl sulphide adsorption sites on which carbon monoxide cannot adsorb and 7.8% of the adsorbed carbon monoxide is less strongly bonded to the rhodium than carbonyl sulphide. When the adsorbents, which were in the steady-state with respect to carbon monoxide adsorption, were saturated with carbonyl sulphide and then had isotopically labeled carbon monoxide pulsed over them, there was significant adsorption and exchange (Table 4). With Rh(O)/silica however there was an unusual effect in that the amount adsorbed from the second pulse was greater than that adsorbed from the first pulse, even though there had been no overall displacement by the first pulse. For this to occur in the absence of displacement requires that there has been a reconstruction of the adsorbed layer either after the adsorption of the first pulse or coincident with the adsorption of the second pulse. This view is reinforced by the amount of carbon monoxide adsorbed, which is greater than the steady-state value; i.e., the sample adsorbs 30% more carbon monoxide than the steady-state value when there is carbonyl sulphide preadsorbed. Note that there was no evidence for such reconstruction when carbon monoxide was pulsed over preadsorbed carbonyl sulphide when the sample was in the steady state with respect to carbonyl sulphide adsorption. Therefore the reconstruction is likely to have involved the material retained during the carbon monoxide adsorption/desorption cycles rather than the adsorbed carbonyl sulphide. If this is indeed the case then it is possible to use the exchange data to estimate the ratio of adsorbed species on the surface. Hence for Rh(O)/silica a ratio of (A) : (B) : (C), 1.4 : 1.2 : 1 is obtained, while for Rh(Cl)/silica an (A) : (B) : (C) ratio of 7.2 : 1 : 2.9 is obtained, indicating a higher degree of partial dissociation on the Rh(O)/silica.

CONCLUSIONS

Three distinct forms of adsorbed carbonyl sulphide have been detected. The ratio of the amounts of these species is dependent upon the metal crystallite particle size and species already present on the surface. On a sample produced from rhodium trichloride, sites were found that would adsorb carbonyl sulphide but not carbon monoxide.

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