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NOTES

The Effect of Pre-adsorbed Sulphur on Carbon Monoxide Hydrogenation over Rhodium/Silica

There has been considerable interest in the hydrogenation of carbon monoxide over rodium catalysts over the last 10–15 years, and a significant amount of research effort, both academic and industrial, has gone into methods of increasing both the selectivity and activity of these catalysts (*1*). According to the literature it is possible to enhance the rate of carbon monoxide hydrogenation and to affect the selectivity by the addition of a modifier to the silica support (*2*). However, another method which may be used is modification of the rhodium, after reduction, by a suitable adsorbate. Hence we embarked on a short programme of work aimed at studying the effect of pre-adsorbed sulphur, deposited from hydrogen sulphide and carbonyl sulphide, on the activity and selectivity of rhodium-catalysed carbon monoxide hydrogenation.

A 1.2% w/w Rh/silica catalyst was prepared by aqueous impregnation using rhodium trichloride. All reductions were carried out *in situ* by heating the sample in a stream (100 cm^3 min^{-1}) of 4 : 1 nitrogen : hydrogen to 573 K and holding at this temperature for 0.5 h. The apparatus used for both the adsorption and reaction studies have been detailed elsewhere (*3, 4*). The amounts of carbon monoxide, hydrogen sulphide, and carbonyl sulphide adsorbed on a freshly reduced catalyst were 131.7 μmol $(g_{cat})^{-1}$, 74.5 μmol $(g_{cat})^{-1}$, and 32.6 μmol $(g_{cat})^{-1}$, respectively. Sulphur was pre-adsorbed on the reduced catalysts by pulsing sufficient hydrogen sulphide or carbonyl sulphide, at 293 K, to produce 5, 10, 20, and 40% of a monolayer (Table 1) as determined from the above adsorption data. It should be noted that approximately equivalent amounts of sulphur were deposited when the percentage of monolayer coverage from the hydrogen sulphide was half that of the carbonyl sulphide, e.g.-, 5% of a monolayer of hydrogen sulphide deposited an amount of sulphur equivalent to that deposited by 10% of a monolayer of carbonyl sulphide. Following this the catalysts were transferred to the previously described medium pressure microreactor system and re-reduced. Test reductions in an all-glass system with on-line GC–MS indicated that no sulphur-containing compounds were desorbed during the re-reduction process.

Each catalyst exhibited a typical period (approximately 1 h) of non-steady-state behaviour (*4*) immediately after coming on stream before settling to steady-state operation. Once steady-state conditions had been achieved, reproducible activities and selectivities were observed. Activities and selectivities obtained at 548 K are shown in Fig. 1 and 2 and Table 2. The test conditions are also detailed in Table 2.

On pre-adsorption of 5% of monolayer of hydrogen sulphide the yield of all the hydrocarbon species was decreased. Similarly the oxygenate species which rely on hydrocarbon intermediates, i.e., all except methanol, were also reduced by proportionally similar amounts, e.g., ethane production was reduced by 77% while ethanol production was reduced by 65%. However, the activity for methanol production increased by 68%. This can be rationalised by the electronegative effect of sulphur inhibiting the dissocia-

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TABLE 1

Amount of H_2S and COS Pre-adsorbed[a]

Adsorbing gas	Amount adsorbed (% of monolayer)			
	5%	10%	20%	40%
H_2S	3.7	7.5	14.9	—
COS	1.6	3.3	6.5	13.0

[a] Units; μmol $(g_{cat})^{-1}$.

tion of adsorbed carbon monoxide (5). The production of methanol from carbon monoxide has been shown by isotopic tracer studies (6) to involve non-dissociated carbon monoxide; therefore an increase in associatively adsorbed carbon monoxide, and no effect on the hydrogen concentration, would allow an enhancement in the rate of production of methanol. At 10% of a monolayer of pre-adsorbed hydrogen sulphide the main effect was the loss of methanol yield; surprisingly there was little or no effect on the other products. A change in the operation of the poison from a principally electronic effect to one of site blocking could result in such behaviour, but it would have been expected that rather than a switch from one type of poisoning behaviour to another a combination effect would be observed. At 20% of a monolayer the catalyst lost nearly all activity. The near-total loss in activity at this level of sulphur can be predicted using the equation developed by Joyner and Pendry (7). Using their method 10.7 μmol $(g_{cat})^{-1}$ of sulphur should be sufficient to totally poison the catalyst, which is in good agreement with that deposited from the 20% of a monolayer hydrogen sulphide (14.9 μmol $(g_{cat})^{-1}$).

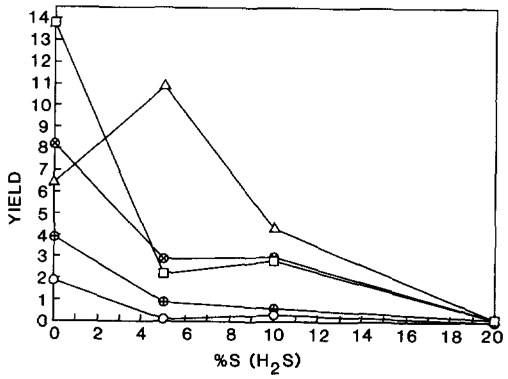

FIG. 1. The variation in yield of the major products with amount of sulphur coverage, as deposited from hydrogen sulphide. (□) $CH_4/10$, (⊕) C_2H_6, (○) $C_3 - C_4$, (△) CH_3OH, (⊗) C_2H_5OH.

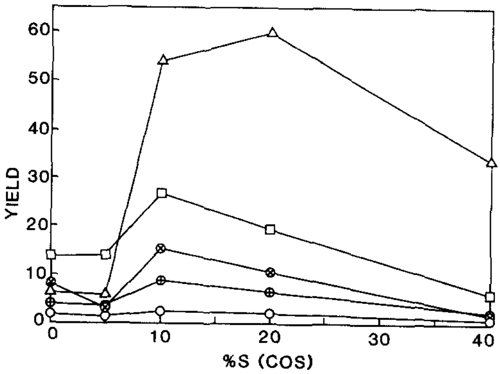

FIG. 2. The variation in yield of the major products with amount of sulphur coverage, as deposited from carbonyl sulphide. (□) $CH_4/10$, (⊕) C_2H_6, (○) $C_3 - C_4$, (△) CH_3CHO, (⊗) C_2H_5OH.

At 5% of a monolayer of carbonyl sulphide there was only a slight loss in activity due principally to a decrease in oxygenate formation. However, at 10% of a monolayer of pre-adsorbed carbonyl sulphide there was an *enhancement* of activity of all products except methanol. This was a surprising result as the quantity of sulphur deposited was similar to that obtained with 5% of a monolayer of hydrogen sulphide, which resulted in a considerable decrease in catalyst activity. At 20% of a monolayer of carbonyl sulphide this enhanced activity was maintained although the level had decreased from that obtained at 10% of a monolayer of carbonyl sulphide. At 40% of a monolayer (equivalent in sulphur deposition to 20% of a monolayer of hydrogen sulphide) the activity of the majority of

TABLE 2

Activities and Selectivities Observed for Pre-adsorbed Sulphur Modified Catalysts[a]

%S	Source of sulphur	Major products[b]														Total activity	Total oxygenate selectivity (%)
		CH_4		C_2H_6		$C_3 - C_4$		CH_3OH		C_2H_5OH		CH_3CHO		MeAc			
		Y	S	Y	S	Y	S	Y	S	Y	S	Y	S	Y	S		
0	—	137.2	70	3.9	4	1.9	3	6.5	3	8.2	8	6.4	7	0.7	1	166.6	22
5	H_2S	22.1	49	0.9	4	0.1	1	10.9	24	2.9	13	0.0	0	0.1	1	38.0	46
10	H_2S	28.0	65	0.6	3	0.3	2	4.3	10	3.0	14	1.1	5	0.1	1	37.5	30
20	H_2S	1.1	64	0.1	14	0.0	4	0.1	4	0.1	14	0.0	0	0.0	0	1.5	18
5	COS	139.2	78	3.5	4	1.4	3	4.3	2	3.1	4	5.8	4	0.7	1	159.1	15
10	COS	267.8	58	8.9	4	2.5	2	0.0	0	15.5	7	53.8	23	4.3	3	357.9	37
20	COS	195.2	52	6.6	4	2.1	2	0.0	0	10.7	6	59.8	32	1.9	2	280.1	43
40	COS	61.6	39	2.4	3	0.9	2	0.0	0	1.8	2	33.7	42	2.2	4	106.0	57

[a] Conditions: $CO : H_2$, 1 : 2; pressure 1.01 MPa; temperature 548 K; GHSV 1200 h^{-1}; sample weight 0.5 g.
[b] Y, yield nmol $(g_{cat})^{-1} \cdot s^{-1}$; S, selectivity percentage; MeAc, CH_3OOCCH_3.

the products had decreased to below that observed when no sulphur was present; the notable exception was ethanal, the yield of which was still a factor of five greater than from the non-poisoned catalyst.

Enhancement of reaction rate when sulphur has been added to a system is rare, but it has been observed previously. For example, in platinum-reforming catalysis the addition of sulphur has been shown, by Shum *et al.* (*8*), to result in a higher rate of reaction. Such enhancement may be due to a change in the mechanism of reaction due to the effect of pre-adsorbed sulphur. Therefore the reaction mechanism was probed using isotopically labelled carbon monoxide in a manner identical to that carried out previously (*9*). The behaviour of the isotopes in the system mirrored that obtained on non-sulphide-containing catalysts, indicating that there had been no change in mechanism or residence time of the surface intermediates. Equally no significant change was observed in apparent activation energies (for the non-poisoned catalyst; methane, 100 kJ mol^{-1}, ethanal, 54 kJ mol^{-1}, for the carbonyl sulphide-poisoned catalysts; methane, 97 kJ mol^{-1}, ethanal, 57 kJ mol^{-1}). Therefore the sulphur must be modifying the catalyst in such a way as to increase the concentration of adsorbed intermediates.

One means by which such an increase may be achieved is by surface reconstruction resulting in a higher concentration of suitable adsorption sites. This can be seen most clearly in the case of aldehyde production, which, from the mechanisms proposed by Orita *et al.* (*10*) and Jackson *et al.* (*9*), requires a unique site. Therefore to achieve an enhancement of ethanal yield it is necessary for structural reconstruction to allow an increase in suitable sites. Although there is little reported work on carbonyl sulphide adsorption (*11*) the literature does indicate that different sulphur species do cause different responses in crystallite structure. Bergeret and Gallezot (*12*) studied the effect of hydrogen sulphide, sulphur dioxide, and elemental sulphur adsorption on the structure of platinum crystallites. They stated that "the modification of the aggregate structure depends upon the nature of the sulphur compound," and found that hydrogen sulphide had the smallest effect of the three sulphur species studied. Therefore it is not unreasonable that carbonyl sulphide adsorption should cause a surface reconstruction which would be different from that caused by hydrogen sulphide adsorption. Hence the effect of carbonyl sulphide on the catalyst's activity and selectivity can be understood in terms of surface structure modification resulting in increased concentration of adsorbed intermediates.

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