JOURNAL OF CATALYSIS **150**, 170–176 (1994)

The Effect of Sulphur on the Nonsteady State Reaction of Propane over a Platinum/Alumina Catalyst at 873 K

S. D. Jackson,[1] P. Leeming, and J. Grenfell

ICI Katalco, Research Technology & Engineering Group, P.O. Box 1, Billingham, Cleveland TS23 1LB, United Kingdom

Received November 19, 1993; revised March 18, 1994

The addition of sulphur to Pt/alumina catalysts, both in the preparation stage and in the gas phase during reaction, has been investigated as to the effect on catalyst activity and selectivity for propane dehydrogenation. The sole hydrocarbon product produced from pulses of propane over a freshly reduced Pt/alumina catalyst at 873 K in the absence of sulphur was methane, with concomitant carbon laydown. The effect on activity and selectivity of predosing the catalyst with hydrogen sulphide at 293 and 873 K was examined, as was the effect of cofeeding at ratios of 1:10 and 10:1 $H_2S:C_3H_8$. Predosing at 873 K had the largest effect on selectivity, allowing the formation of propene from the first pulse of propane, whereas cofeeding required the build-up of sulphur on the surface before selectivity was achieved. Adding sulphur into the catalyst preparation was more effective than subsequent addition from the gas phase. The results also indicated that the selectivity observed was not directly related to the amount of sulphur on the surface. The presence of a hydrogen reservoir on the catalyst, which was available for reaction, was detected using catalysts reduced in deuterium. The results also indicated that hydrogen from adsorbed hydrogen sulphide could react with hydrocarbon fragments on the catalyst surface to produce methane. © 1994 Academic Press, Inc.

INTRODUCTION

Sulphur is defined as a nonspecific catalyst poison and can dramatically reduce catalytic activity (for a general review see Ref. (1)). However, at low concentrations it has been used to modify catalytic properties, especially selectivity. For example, the addition of sulphur in platinum-catalysed reforming reduces the amount of carbon laydown and increases the rate of reaction (2). It is further held that in reforming over Pt–Re/alumina sulphur enhances the aromatization reaction (3). The effects of sulphur on catalyst selectivity are well documented in the area of carbon monoxide hydrogenation (4–7). In the case of carbon monoxide hydrogenation over Rh/silica, the addition of sulphur results in an eightfold increase in the selectivity to methanol (4). 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 addition of 10 ppm hydrogen sulphide to the feedstream results in the methane yield falling from 100 to 58% and the C_2 yield increasing from 0 to 42%. The authors of this latter work concluded that sulphur poisoned the ability of the surface to hydrogenate more severely than the ability to form carbon–carbon bonds (7). In the area of synthesis gas production via steam reforming of hydrocarbons over nickel catalysts, the poisoning of activity due to sulphur has been thoroughly examined by Rostrup-Nielsen and Højlund-Nielsen (8).

In propane dehydrogenation, the continuous addition of sulphur in steady-state operation to a $Pt/MgAl_2O_4$ catalyst has been shown to reduce coke formation and increase selectivity to propene (9). However, the system was shown to be sensitive to the support used; when alumina was the support the addition of sulphur reduced both selectivity and conversion. The system was further complicated by the cofeeding of hydrogen. In our studies of propane dehydrogenation over a Pt/alumina catalyst we observed that, upon initial use, there was nonsteady state behaviour where there was little or no selectivity to the alkene and significant carbon laydown. A reduction in the amount of carbon laydown, especially in the early stages of catalyst life, would have considerable benefits in plant operation, as would minimising the period of zero selectivity to the alkene. Therefore we undertook this study to assess whether the addition of sulphur, from hydrogen sulphide, either by addition to the feedstream or by predosing, could enhance the initial activity/selectivity of a Pt/alumina catalyst when used for propane dehydrogenation.

EXPERIMENTAL

Apparatus and Procedures

Reaction studies were performed in a dynamic mode using an all-glass, 0.101 MPa, pulse-flow microreactor system, incorporating on-line GC-MS, in which the cata-

---

[1] To whom correspondence should be addressed.

0021-9517/94 $6.00

lyst sample was placed on a sintered glass disc in a vertical tube (8 mm i.d.) inside a furnace. Using this system the catalysts (typically 0.3–0.5 g) could be reduced *in situ* in flowing 5% hydrogen in nitrogen or deuterium (50 cm^3 min^{-1}) by heating to 873 K at 10 K min^{-1} and then holding at this temperature for 0.25 h. After reduction had ceased the catalyst was maintained, at the desired temperature, in flowing helium (70 cm^3 min^{-1}). The adsorbate (hydrogen sulphide) or reaction gas (propane) was admitted by injecting pulses of known size (typically 1.72 cm^3, 6.67 × 10^3–3.99 × 10^4 Pa) into the helium carrier-gas stream and hence to the catalyst. After passage through the catalyst bed the total contents of the pulse were analysed by GC-MS. The amount of gas adsorbed or reacted, from any pulse, was determined from the difference between calibration peak areas of the gases and the peak areas obtained following the injection of pulses of comparable size onto the catalyst. Adsorption, desorption, and reaction were followed using a gas chromatograph fitted with a thermal conductivity detector and Porapak Q-S column coupled to a mass spectrometer (Spectramass SM100D).

Materials

The catalyst used throughout this study was 0.66% Pt/alumina. The catalyst was prepared by impregnation of the alumina (Harshaw, 100 m^{2}g^{-1}) with the required amount of chloroplatinic acid solution to achieve the desired weight loading. The material was dried and then calcined in air at 823 K for 3 h. After reduction as outlined above, a sample of catalyst was cooled to 293 K and the carbon monoxide adsorptive capacity measured. The amount of carbon monoxide adsorbed was 1.573 × 10^{19} molecules g^{-1}, giving a dispersion, assuming a 1 : 1 CO : Pt ratio, of 77%. Two further catalysts were prepared as above but with sulphuric acid (BDH AristaR) added to the impregnating solution. The platinum loading was analysed at 0.62% w/w Pt for both samples, with sulphur loadings of 3.4% w/w and 30 ppm, respectively.

Both the helium (Air Products, 99.998%) and the 5% hydrogen in nitrogen (ICI) were further purified by passing through a bed of reduced Pd/WO$_3$ to remove any oxygen impurity, and a bed of Carbosorb AS (BDH) to remove any water impurity. The hydrogen sulphide and propane (both BDH) were further purified using a freeze/thaw technique.

RESULTS AND DISCUSSION

Hydrogen Sulphide Adsorption

Pulses of hydrogen sulphide were passed over the catalyst at 10-min intervals until the catalyst was saturated (Table 1). Once adsorption had ceased, the catalyst was heated to 873 K in flowing helium and the desorption noted (Table 1). From the literature (10–12) and our own studies on other systems (13) it was known that hydrogen sulphide adsorbs on both the metal and the alumina support, and indeed the high S : Pt ratio was a reflection of this (Table 1). The thermal desorption indicated that approximately half of the material adsorbed at 293 K was desorbed by 873 K.

TABLE 1

Hydrogen Sulphide Adsorption on Pt/Alumina at 293 K

Initial adsorption (×10^{19})	S : Pt	Amount[a] desorbed (%)	Amount[b] readsorbed (×10^{19})
21.69	10.6 : 1	43.2 (558 K) 1.4 (741 K) 4.6 (823 K)	17.65

[a] The amount desorbed expressed as a percentage of the amount adsorbed. The temperature in parentheses indicates the desorption temperature.

[b] The amount of hydrogen sulphide readsorbed at 293 K after the thermal desorption procedure.

As hydrogen is produced in propane dehydrogenation, the reactivity to hydrogen of the sulphur species, retained at 873 K, was investigated. When no further desorption was detected, aliquots of deuterium, viz. [^{2}H]dihydrogen, were pulsed over the catalyst at 873 K. Hydrogen sulphide, as [^{2}H]hydrogen sulphide, [^{1}H, ^{2}H]hydrogen sulphide, and [^{1}H]hydrogen sulphide, was detected by mass spectrometry. The amount of [^{1}H, ^{2}H]hydrogen sulphide was greater than the amount of [^{2}H]hydrogen sulphide in the eluent gas. The result of treating the catalyst with [^{2}H]dihydrogen at 873 K showed that the retained sulphur was resistant to removal by hydrogen, with only trace quantities of hydrogen sulphide being detected. The results also indicated that the sulphur is bonded to hydrogen (principal desorption product being [^{1}H, ^{2}H]hydrogen sulphide). These results are in agreement with the results of Ponitzsch et al. (12) where, after adsorption at 623 K, only a small hydrogen sulphide desorption was detected in helium but a larger amount was desorbed in the presence of hydrogen.

The catalyst was subsequently cooled to 293 K and hydrogen sulphide readsorbed (Table 1). The readsorption of hydrogen sulphide was greater than the measured loss from the thermal desorption and the treatment with hydrogen. This suggests mobility of the surface sulphur species from the adsorption sites so allowing further adsorption; it also indicates that the majority of the thermally desorbed material was adsorbed on the alumina.

Propane Dehydrogenation in the Absence of Sulphur

Immediately after reduction the catalyst was subjected to pulses of propane at 873 K. The results are shown in

TABLE 2

The Dehydrogenation[a] of a 1 : 1 Mix of C_3H_8 : [^{2}H]C_3H_8 over Pt/Alumina Reduced in [^{2}H]Dihydrogen, i.e., Deuterium D_2

Pulse No.	CH_4[b]	Isotope distribution (%)				
		CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
1	100	0	0	5	30	64
2	79	0	3	34	41	22
3	66	0	13	43	34	10
4	60	0	20	43	29	7
5	54	0	39	36	21	5

[a] Conditions: temperature 873 K, GHSV 7778 h^{-1}.

[b] Methane was the sole gaseous product. Percentage calculated on carbon basis, i.e., in pulse 2, 79% of the inlet carbon was detected as methane in the exit gas. The difference between the sum of the components and 100% represents the amount of carbon deposition.

Table 2. The only detectable gaseous product was methane. The experiment was repeated with a catalyst which had been reduced in [^{2}H]dihydrogen using a 1 : 1 mix of C_3H_8 : [^{2}H]C_3H_8. The isotopic distribution results are also presented in Table 2 and show a bias towards methane containing [^{2}H]hydrogen. These results indicate that the catalyst retains [^{2}H]hydrogen from the reduction process and that this [^{2}H]hydrogen is reactive.

The typical reactions that can occur during the interaction of propane with the catalyst are:

$$C_3H_8 \rightarrow 2CH_4 + C \qquad [1]$$

$$C_3H_8 \rightarrow CH_4 + C_2H_4 \qquad [2]$$

$$C_3H_8 \rightleftharpoons C_3H_6 + H_2 \qquad [3]$$

$$C_3H_8 \rightarrow 3C + 4H_2 \qquad [4]$$

Although formally all the reactions are equilibria, only Eq. [3] is measurably reversible under reaction conditions. The amount of methane formed from pulse 1 (approximately 100%) was more than would be predicted if all the propane reacted according to Eq. [1], which would give a yield of methane of 66%. This higher value for methane indicated that there was hydrogen retained by the catalyst after reduction. This was confirmed by the isotope studies (Table 2), which showed that approximately 4×10^{20} [^{2}H]hydrogen atoms g^{-1} were used in the production of methane, over the course of the five pulses. In pulses 1–4 there was a net gain of [^{2}H]hydrogen, whereas there was a net loss of [^{1}H]hydrogen in all five pulses. In terms of hydrogen mass balance for each pulse, we found that there was an overall hydrogen gain in pulses 1 and 2 and loss of hydrogen in pulses 3–5. Even by pulse 5 the system had not reached equilibrium. This retention of hydrogen by a platinum catalyst during reduction, and its subsequent liberation, has been observed before (14–16). The product distribution from subsequent pulses indicates that the dominant reaction in these initial stages was reaction [1] with a contribution from reaction [4]. These results showed that the catalyst was highly active (100% conversion of propane) but had no inherent selectivity to propene in the initial stages of operation. The results also showed that the carbon laydown does not affect the selectivity of the system during the time that we were examining the catalyst.

Effect of Preadsorption of Hydrogen Sulphide on Propane Dehydrogenation

When hydrogen sulphide was preadsorbed at 293 K and the sample heated to 873 K, a proportion (approximately 50%) of the adsorbed species desorbed as hydrogen sulphide as described above and shown in Table 1. When propane was then pulsed over this catalyst there was no desorption of hydrogen sulphide but there was a considerable change in the product distribution compared to that obtained from a clean catalyst (Table 3, cf. Table 2). The major gaseous product was still methane but both ethane and ethene were formed. The amount of carbon deposition from the first pulse was higher at 20%, but by pulse 5 the carbon deposition had decreased from 46%, in the absence of sulphur, to 20% after hydrogen sulphide adsorption. The increase in carbon laydown in the first pulse can be ascribed to the lower amount of catalyst-retained hydro-

TABLE 3

Propane Dehydrogenation[a] after Hydrogen Sulphide Preadsorption at 293 K

Pulse No.	Product distribution (%)[b]		
	CH_4	C_2H_4	C_2H_6
1	73	4	4
2	71	1	2
3	71	2	2
4	71	1	1
5	79	1	2
6	77	2	1

[a] Conditions: temperature 873 K, GHSV 7778 h^{-1}.

[b] Percentage calculated on carbon basis, i.e., in pulse 1, 73% of the inlet carbon was detected as methane in the exit gas. The difference between the sum of the components and 100% represents the amount of carbon deposition. No propene or propane was detected in any of the pulses.

gen available for reaction. This was shown by the isotope profile of the methane, which was found to be significantly different from those obtained in the absence of the preadsorbed hydrogen sulphide, i.e., pulse 1, 8% CD_2H_2, 19% CDH_3, and 73% CH_4, and for pulse 2, 3% CD_2H_2, 6% CDH_3, and 91% CH_4. From the previous study (14) on this type of hydrogen it is known that chemisorption of a strongly adsorbing species can cause the desorption of this hydrogen. Therefore it appears that adsorption of hydrogen sulphide at 293 K is sufficient to reduce the amount of hydrogen retained and hence available for reaction.

The decrease in the amount of carbon laydown, in the later pulses, was dramatic and indicates that sulphur was poisoning the carbon deposition reaction. For methane production, on the other hand, the yield increased in the later pulses, indicating that the adsorbed sulphur species acted as a promoter. These effects are similar to those observed by Shum *et al.* (2) for the effect of sulphur in hydrocarbon reforming. However, there is another aspect which should be noted; the methane yield was maintained, over the six pulses, above the level possible by hydrogen only being supplied by the propane. As shown earlier, there was residual hydrogen associated with catalyst which was involved in the production of methane. However, it can be seen from Table 3 that the methane yield was held above the theoretical maximum for all six pulses, whereas in Table 2 the methane yield was only above this value in the first two pulses. Also the isotopic profile of the methane from the later pulses showed no evidence of [^{2}H]hydrogen. From the experiment where [^{2}H]hydrogen was pulsed over a sample containing retained hydrogen sulphide, it was shown that the adsorbed sulphur species contained significant quantities of hydrogen. Therefore hydrogen from the retained hydrogen sulphide moiety is the most likely source of the excess hydrogen.

The experiment was repeated but with the hydrogen sulphide being preadsorbed at 873 K rather than 293 K. When the first pulse of propane was passed over this catalyst, hydrogen sulphide was desorbed and a propane dehydrogenation product distribution which contained both propene and propane was observed (Table 4). The amount of hydrogen sulphide desorbed represents only 9% of that initially adsorbed, but if that portion was solely adsorbed on the metal function then it would represent 0.56 of a monolayer as calculated from the amount of carbon monoxide adsorption, which is similar to the value of 0.51 reported by Bechtold (17) for saturation of polycrystalline Pt by sulphur at 723 K. The effect of the loss of that hydrogen sulphide is seen in the product distribution from the second pulse, when no propene or propane were detected and the production of methane increased. Isotopic analysis of the methane revealed 3% CD_2H_2, 6% CDH_3, and 91% CH_4 for pulse 2 (results were not obtained from pulse 1). However, in comparing Tables 3 and 4 it is apparent that preadsorption of hydrogen sulphide at reaction temperature was more effective at limiting methane formation and promoting formation of ethene and propene, even after the hydrogen sulphide loss on the first propane pulse, than preadsorption at 293 K and heating to 873 K. It should be appreciated that there was considerably more hydrogen sulphide retained by the catalyst at 873 K, after adsorption at 293 K, than after adsorption at 873 K (1.28 × 10^{19} molecules g^{-1}). Therefore hydrogen sulphide adsorption at high temperature is having a larger effect on propane dehydrogenation activity/selectivity than hydrogen sulphide adsorption at 293 K. Hence the absolute quantity of sulphur on the catalyst does not, in itself, determine poisoning efficiency.

TABLE 4

Propane Dehydrogenation[a] after Hydrogen Sulphide Preadsorption at 873 K[b]

Pulse No.	Product distribution (%)[c]				
	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
1[d]	50	5	10	4	8
2	60	4	6	0	0
3	55	4	4	0	0
4	51	6	5	0	0

[a] Conditions: temperature 873 K, GHSV 7778 h^{-1}.

[b] Amount of hydrogen sulphide adsorbed, 9.744 × 10^{19} molecules g^{-1}.

[c] Percentage calculated on carbon basis, i.e., in pulse 1, 50% of the inlet carbon was detected as methane in the exit gas. The difference between the sum of the components and 100% represents the amount of carbon deposition.

[d] Amount of hydrogen sulphide desorbed when first pulse of propane was passed over the catalyst, 8.82 × 10^{18} molecules g^{-1}.

Effect of Coadsorption of Hydrogen Sulphide on Propane Dehydrogenation

Immediately after reduction in [^{2}H]dihydrogen, aliquots of pre-mixed propane and hydrogen sulphide, having a 1 : 10 $H_2S : C_3H_8$ ratio, were passed over the catalyst at 873 K (Table 5). Two aspects of the results are immediately apparent; (i) all the hydrogen sulphide was adsorbed, and (ii) methane was the only gaseous hydrocarbon product. The amount of methane produced, over the first four pulses, was similar to that observed when propane was passed over the catalyst in the absence of hydrogen sulphide and analysis of the isotope distribution in the methane (Table 5, pulses 1 and 2, cf. Table 2, pulses 1 and 2) also showed similarities. Therefore, over the first four pulses the hydrogen sulphide was having very little effect on the activity/selectivity of the system. However, the yield of methane increased in pulse 5 suggesting, as was

TABLE 5

Propane Dehydrogenation[a] in the Presence of Gas Phase Hydrogen Sulphide at a Ratio of 1:10 $H_2S:C_3H_8$

Pulse No.	H_2S out (%)	CH_4[b]	Isotope distribution (%)				
			CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
1	0	90	0	0	7	20	73
2	0	83	0	0	59	28	13
3	0	68	23	34	32	11	0
4	0	63	[c]				
5	0	78	[c]				
6	0	66	[c]				

[a] Conditions: temperature 873 K, GHSV 7778 h^{-1}.
[b] Percentage calculated on carbon basis.
[c] Data not available.

detailed earlier, that hydrogen sulphide was facilitating the production of methane by donating hydrogen. Even so, there was insufficient sulphur adsorbed to affect the selectivity of the catalyst in terms of propene production.

When the experiment was repeated using a 10:1 $H_2S:C_3H_8$ ratio (Table 6), the adsorption of hydrogen sulphide over the sequence of pulses gave a standard shaped isotherm, similar to that obtained when hydrogen sulphide was adsorbed at 873 K in the absence of propane. On the first pulse the production of methane was similar to that in the absence of hydrogen sulphide; however, by pulse 2 the amount of methane produced halved, and by pulse 3 the methane yield was approximately one-third that of pulse 2. At the same time the amount of unreacted propane was increased, as was the amount of propene and C_2's. Therefore, as the amount of surface sulphur increased so the activity decreased and the selectivity to propene increased. This is in contrast to the results found by Rennard and Freel (9), in the steady state, where the selectivity decreased along with conversion.

TABLE 6

Propane Dehydrogenation[a] in the Presence of Gas Phase Hydrogen Sulphide at a Ratio of 10:1 $H_2S:C_3H_8$

Pulse No.	H_2S out (%)	Product distribution (%)[b]				
		CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
1	0	95	0	0	0	0
2	15	48	0	0	0	0
3	46	17	0	0	0	tr[c]
4	56	11	tr	tr	3	72
5	69	10	tr	tr	4	81

[a] Conditions: temperature 873 K, GHSV 7778 h^{-1}.
[b] Percentage calculated on carbon basis.
[c] tr, trace.

TABLE 7

Effect of Sulphuric Acid Added in Catalyst Preparation on Propane Dehydrogenation[a]

Pulse No.	Product distribution (%)[b]						
	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
Sulphur level: 30 ppm							
1	0	0	61	0	0	0	0
2	0	0	55	0	0	0	0
3	0	0	55	0	0	0	0
4	0	0	53	0	0	0	0
5	0	0	46	0	0	0	0
Sulphur level: 3.4%							
1	3	20	1	3	12	12	21
2	1	3	11	3	10	15	29
3	1	2	9	3	7	16	33
4	1	1	6	3	4	20	47
5	0	1	4	3	3	21	56

[a] Conditions: temperature 873 K, GHSV 7778 h^{-1}.
[b] Percentage calculated on carbon basis.

Effect of Using Catalysts Prepared with Sulphuric Acid

From Table 7 it can be seen that when the catalyst with the low level of sulphur (5.6×10^{17} S atoms g^{-1}) was tested, the sample behaved as though no sulphur was present, i.e., methane was the sole product. This was in keeping with the gaseous adsorption results where even with sulphur levels two orders of magnitude higher the catalyst was still selective solely to methane. However, when the high level sulphur sample (6.396×10^{20} S atoms g^{-1}) was tested, it immediately produced propene with a selectivity far higher than that achieved by the other methods. This level of sulphur was approximately six times that achieved via the adsorption methods and will, most probably, be in a different chemical state (sulphate rather than sulphide). However, the state of the sulphur or indeed the platinum in this catalyst may not be readily ascertained (18, 19). The production of carbon monoxide and carbon dioxide suggests that a fraction of the sulphur species present was reduced to a lower oxidation state (approximately 5% if the process was $SO_4 \rightarrow SO_3$).

CONCLUSIONS

On comparing the effect of the amount of adsorbed sulphur on the dehydrogenation activity/selectivity of Pt/alumina catalyst between preadsorption and coadsorption of sulphur species, considerable differences are noted. In Table 3, pulse 1, 1.116×10^{20} molecules g^{-1} of hydrogen sulphide had been retained at 873 K following preadsorption at 293 K, while in Table 4, pulse 1, 8.862×10^{19} molecules g^{-1} of hydrogen sulphide had been retained at 873 K after pre-adsorption at 873 K. In contrast, by pulse 5 in Table 6, 4.504×10^{19} molecules g^{-1} of hydrogen sulphide had been retained from cofeeding propane and hydrogen sulphide at 873 K. These levels of sulphur are accompanied by changes in the activity/selectivity achieved by the catalyst. Contrary to the obvious expectation, as the amount of sulphur decreased the selectivity increased, indicating that the method of adsorption was more important than the amount adsorbed. The results from adding sulphuric acid to the catalyst preparation show that incorporating sulphur in this way was more effective at generating selectivity to propene than an adsorption method. Why this should be the case is not entirely clear. From the results (Table 7) we can surmise that the oxidised sulphur is being reduced; however, the final state cannot be determined from these experiments. Indeed, there has been some debate in the literature (18, 19) over the electronic state of the platinum when sulphate is present and changes in the electron density at sites on the platinum crystallite would undoubtedly have an effect on the activity and selectivity of the system. Further study of these systems is required by a range of surface science and catalysis techniques before an unambiguous assignment can be made.

The reaction of propane to methane (Eq. [1]) was the reaction most affected by the presence of sulphur on the catalyst. On small crystallites such as the ones present on the catalyst used in this study (approximate particle size 1.4 nm, average coordination number 7.5), reactions such as hydrogenolysis have been shown to take place on corners and edges (20, 21). Therefore the activity of the catalyst towards hydrogenolysis can be dramatically affected by selective poisoning of corner and edge sites. Indeed, this is the basis of the addition of sulphur in hydrocarbon reforming (22) where the sulphur selectively poisons the undesired reactions. The position of adsorbed sulphur on small crystallites is not unambiguously defined; however, it is generally agreed that the sulphur adsorbs on sites with the highest bond strength (12, 23) and studies by Glowski and Madix (24) and by Somorjai and Blakely (25) indicate that these sites are corner and edge atoms. Note that on large crystallites both the sites for hydrogenolysis and sulphur adsorption may differ from those on small crystallites (1, 22, and 23). Therefore, in this description of the poisoning effect, the quantity of poison adsorbed is not in itself the primary consideration, rather is it the adsorption site which is of critical importance. The adsorption of sulphur, however, does not solely decrease the conversion of propane to methane: it also apparently increases the rate of dehydrogenation. This increase in propene activity may be explained by the following. If it can be assumed that there are always sites which will transform propane into propene present on the catalyst, then the lack of selectivity may be due to secondary reaction of the propene after desorption and readsorption on a hydrogenolysis site, or the adsorbed propane/propene may be mobile on the surface and without desorbing transfer to the hydrogenolysis site. Either way the result would be the same in that no propene would be observed to exit the reactor. It is also possible to explain the enhancement of propene yield via the ability of sulphur to induce surface restructuring and hence generate sites, which may not initially have been present on the surface (26–28). Although this latter explanation would appear to be less convincing, results from other studies on a similar system (29, 30) may support such a hypothesis.

Other surprising aspects of this study were (i) the retention of hydrogen by the catalyst and its subsequent availability for reaction, and (ii) the donation of hydrogen from the hydrogen sulphide to sustain high methane yields. When retained hydrogen was present on the catalyst, carbon laydown could be reduced to zero and methane formation maximised. These effects are to be expected once it is appreciated that there is a large standing concentration of reactive hydrogen on the surface. Such hydrogen has been detected in two previous studies. One study, using a similar catalyst (the alumina support was different) (14), but not after such high temperature treatment, produced limited evidence (15) which indicated that the hydrogen could be used for hydrogenation. The other study (29), which also involved propane dehydrogenation, confirmed that the catalyst did retain hydrogen from the reduction process and was available for reaction with adsorbed hydrocarbon. The use of the hydrogen associated with the adsorbed sulphur as a source of hydrogen for hydrogenation was also unexpected. Although the mode of hydrogen sulphide adsorption is dissociative, leading to the release of hydrogen (31), our results have shown that all of the hydrogen is not desorbed. We believe that this is the first time that it has been shown that hydrogen from hydrogen sulphide adsorption has a significant lifetime on the catalyst surface and is able to participate in hydrogenation reactions.

REFERENCES

1. Bartholomew, C. H., Agrawal, P. K., and Katzer, J. R., *Adv. Catal.* **31,** 135 (1981).
2. Shum, V. K., Butt, J. B., and Sachtler, W. M. H., *J. Catal.* **96,** 371 (1985).
3. Menon, P. G. and Prasad, J., *in* "Proc. 6th International Congress on Catalysis" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), Vol. 2, p. 1061. The Chemical Society, London, 1977.
4. Jackson, S. D., Brandreth, B. J., and Winstanley, D., *J. Catal.* **129,** 540 (1991).
5. Madon, R. J., and Shaw, H., *Catal. Rev. Sci. Eng.* **15,** 69 (1977).

6. Herington, E. F. G., and Woodward, L. A., *Trans Faraday Soc.* **35,** 958 (1939).
7. Dalla Betta, R. A., Piken, A. G., and Shelef, M., *J. Catal.* **40,** 173 (1975).
8. Rostrup-Nielsen, J. R., and Højlund Nielsen, P. E., *in* "Deactivation and Poisoning of Catalysts" (J. Oudar and H. Wise, Eds.), p. 259. Dekker, New York, 1985.
9. Rennard, R. J., and Feel, J., *J. Catal.* **98,** 235 (1986).
10. de Rosset, A. J., Finstrom, C. G., and Adams, C. J., *J. Catal.* **1,** 235 (1962).
11. Rosynek, M. P., and Strey, F. L., *J. Catal.* **41,** 312 (1976).
12. Ponitzsch, L., Wilde, M., Tétényi, P., Dobrovolszky, M., and Paál, Z., *Appl. Catal.* **86,** 115 (1992).
13. Jackson, S. D., Leeming, P., and Webb, G., unpublished results.
14. Jackson, S. D., Glanville, B. M., Willis, J., McLellan, G. D., Webb, G., Moyes, R. B., Simpson, S., Wells, P. B., and Whyman, R., *J. Catal.* **139,** 207 (1993).
15. Jackson, S. D., Glanville, B. M., Willis, J., McLellan, G. D., Webb, G., Moyes, R. B., Simpson, S., Wells, P. B., and Whyman, R., *J. Catal.* **139,** 221 (1993).
16. Menon, P. G. and Froment, G. F., *J. Catal.* **59,** 138 (1979).
17. Bechtold, E., *Ber. Bunsenges Phys. Chem.* **70,** 713 (1966).
18. Paál, Z., Muhler, M., and Schlögl, R., *J. Catal.* **143,** 318 (1993).
19. Ebitani, K., Konno, H., Tanaka, T., and Hattori, H., *J. Catal.* **143,** 322 (1993).
20. Brunelle, A. P., Sugier, A., and Le Page, J. F., *J. Catal.* **43,** 273 (1976).
21. Guenin, M., Breysse, M., and Frety, R., *J. Mol. Catal.* **15,** 119 (1984).
22. Biswas, J., Bickle, G. M., Gray, P. G., Do, D. D., and Barbier, J., *Catal. Rev. Sci. Eng.* **30,** 161 (1988).
23. Wise, H., McCarty, J., and Oudar, J., *in* "Deactivation and Poisoning of Catalysts" (J. Oudar and H. Wise, Eds.), p. 1. Dekker, New York, 1985.
24. Glowski, G. E. and Madix, R. J., *Surf. Sci.* **115,** 524 (1982).
25. Somorjai, G. A. and Blakely, D. W., *Nature* **258,** 58 (1975).
26. Bergeret, G. and Gallezot, P., *J. Catal.* **87,** 86 (1984).
27. Huber, H. and Oudar, J., *Surf. Sci.* **47,** 605 (1975).
28. Shih, H. D., Jona, F., Jepsen, D. W., and Marcus, P., *Phys. Rev. Lett.* **46,** 731 (1981).
29. Matheson, I., Webb, G., Grenfell, J., and Jackson, S. D., paper to be presented at the 6th International Symposium on Catalyst Deactivation, Ostend, 1994.
30. Jackson, S. D., Huntington, I., and Grenfell, J., unpublished results.
31. Mathieu, M.-V. and Primet, M., *Appl. Catal.* **9,** 361 (1984).