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Sulphur Poisoning of Ruthenium/Alumina Methanation Catalyst and Hydrogenation of CS_2

N. M. GUPTA, V. S. KAMBLE, AND R. M. IYER

Chemistry Division, Bhabha Atomic Research Centre, Bombay 400085, India

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Different species formed in the interaction of CS_2 with Ru/γ-alumina catalyst in the temperature range 425–625 K were examined using a pulse injection method and a flow microcatalytic reactor. In the presence of H_2 carrier flow, CS_2 reacts over the catalyst to form primarily CH_4 and small amounts of higher hydrocarbons. Prolonged treatment with CS_2 produced new products CO and H_2S from CS_2 and reduced drastically the catalytic methanation of CO. Under the inert atmosphere of He, CS_2 interaction over catalyst generated CO_2 in the initial stage and subsequent H_2 injections gave rise to CH_4. Further CS_2–H_2 injections gave progressively reduced yields of CH_4. At the stage when no methane was formed on H_2 injections following a CS_2 pulse, further injections of CS_2 pulses produced new products, CO, SO_2, COS, and H_2S and subsequent H_2 injections again resulted in H_2S formation. The effect of a time gap between CS_2 and H_2 injections on the yields of CH_4 and H_2S has been studied. XPS studies indicated that CS_2 decomposes on the catalyst surface to give elemental carbon and sulphur. It is suggested that S atoms progressively block those Ru sites where carbon or carbon oxides are methanated. It has also been found that the nascent sulphur formed on decomposition of CS_2 loses its chemical reactivity with increasing temperature and time.

1. INTRODUCTION

The effect of sulphur on methanation and the Fischer–Tropsch (F–T) synthesis reaction has been widely investigated (see review (*1*) and recent publications (*2–5*)). However, most of the published studies mainly deal with the influence of sulphur compounds on yields of different reaction products and detailed information regarding catalyst–poison interactions are not available. In recent years a few attempts have been made to study the mechanisms of the H_2S effect on metal and supported metal catalysts (*6, 7*). CS_2 is another major sulphur-containing product affecting the activity of methanation and F–T synthesis catalysts especially when employed in conversion of coal to hydrocarbons (*8*). An earlier communication from this laboratory (*9*) dealt with the nature and reactivity of intermediate species formed in CO–H_2 and CO_2–H_2 reactions over supported Ru catalysts using a microcatalytic reactor and a method of sequential injection of reactants. By using similar methods, the products formed at different stages in the interaction of CS_2 with γ-alumina and Ru/alumina catalysts have been investigated and the results are reported in this paper. The reactivity towards H_2 of intermediate species formed has also been studied.

2. EXPERIMENTAL

Experimental methods were essentially the same as those described in earlier communications (*9, 10*).

(*a*) *Catalyst.* The catalyst (1.6 wt% Ru/alumina) was prepared by impregnation of γ-alumina (60–80 mesh, BET surface area 197 ± 5 m^2 g^{-1}) with an aqueous solution of $RuCl_3$ followed by drying in air at 400 K and reduction in H_2 at 650 K for 10 hr. The BET area (N_2 adsorption) and active metal area (H_2 chemisorption, details given in Ref. (*9*)) of the catalyst were found to be 180 ± 5 and 7.5 ± 1 m^2 g^{-1}, respectively. One gram of catalyst was taken in a stainless-steel tube reactor (internal diameter 0.4 cm) and was reactivated *in situ* by

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heating in H_2 at 600 K for 3–4 hr. H_2 pretreatments for longer periods up to 20 hr did not alter the experimental results.

X-Ray analysis of both the metal-free alumina and Ru/alumina showed diffraction patterns of γ-Al_2O_3 and AlOOH.

(*b*) *Gas chromatographic and mass spectrometric analysis.* Each experiment consisted of successive injection of 200-μl (STP) pulses of premixed CS_2 vapour and He into the H_2 or He carrier gas stream flowing (32 ml min^{-1}) through the catalyst bed with analysis of effluent gases. Each pulse of 200 μl CS_2/He contained about 1.4 μmole of CS_2. A Porapak-Q column at 296 K and a thermal conductivity detector were used for gas chromatographic analysis of CO, CO_2, CH_4, and H_2S. For CS_2 analysis a column of 10% oxydipropionitrile on Chromosorb was used at 252 K. The gas chromatography data were supplemented with mass spectral analysis carried out using a gc–ms (Micromass 7070) in which the gc column was replaced by the catalyst column.

(*c*) *Surface characterisation.* The catalyst was examined by X-ray photoelectron spectroscopy (XPS) before and after exposure to different amounts of CS_2 vapour. For this purpose, the catalyst pellet (1.2 cm diameter and 0.3 cm thickness) was activated in a glass assembly which could be connected to different gases without exposing the sample to air. The pellet was then heated *in situ* under a He stream at 625 K for 3 hr and then exposed to a He/CS_2 gas mixture (flowing at 10 ml min^{-1}, containing $\approx 6 \times 10^{-5}$ moles CS_2 ml^{-1}). The sample was cooled in He before being transferred to the electron spectrometer. XPS spectra were recorded with Mg$K\alpha$ radiation (1253.6 eV) using a PHI 551 electron spectrometer with computer-controlled data acquisition. Before examination, the sample was left for 15–20 hr in the specimen introduction chamber which was continuously evacuated. The binding energies were referenced to the Au $4f_{7/2}$ (83.8 eV) signal from about 10nm gold film evaporated at the outer edge of the sample pellet and to the O 1*s* (531.6 eV) signal from the alumina matrix.

(*d*) *Gases.* High-purity He from Messrs. Airco was used after further purifying by passing through a unit containing in series Cu (675 K), Ti sponge (1075 K), CuO (675 K) and molecular sieve traps to eliminate any O_2, H_2O, and H_2 impurities present. Electrolytically generated H_2 gas from an Elhygen generator was used after passing it through a Pd/molecular sieve catalyst (425 K) and a molecular sieve trap.

3. RESULTS

(*A*) *Reaction of CS_2 on Catalyst Surface in Presence of H_2 Carrier Gas*

When CS_2 (1.4 μmole) and CO (1.6 μmole) were alternately injected into a H_2 stream flowing over a catalyst, CH_4 formation was observed from both the CS_2 and CO and in both cases the yields of CH_4 increased with catalyst temperature. In mass spectral studies under similar conditions, formation of small quantities (< 10%) of higher hydrocarbons in the C_2–C_4 range from CS_2 was also observed, though no attempt was made to analyse them quantitatively. The typical variation in CH_4 yields with successive CS_2 and CO injections is given in Fig. 1 for the catalyst temperature of 575 K. It is interesting to note that while no CH_4 formed from CO after 22 pulse injections of CS_2 vapour (equivalent to 31 μmole of CS_2 per g of catalyst), the formation of CH_4 from CS_2 continued until much later (Fig. 1). Also, the CH_4 yield from CS_2 increases initially and then shows a decrease at a stage where the poisoning effect for CO methanation was observed. Similar variations in CH_4 yields were observed at other catalyst temperatures, the amount of CS_2 required to poison the catalyst for CO methanation being 28–35 μmole in each case.

At the stage where no CH_4 was formed from CO injections, further injections of CS_2 pulses gave rise to the two new prod-

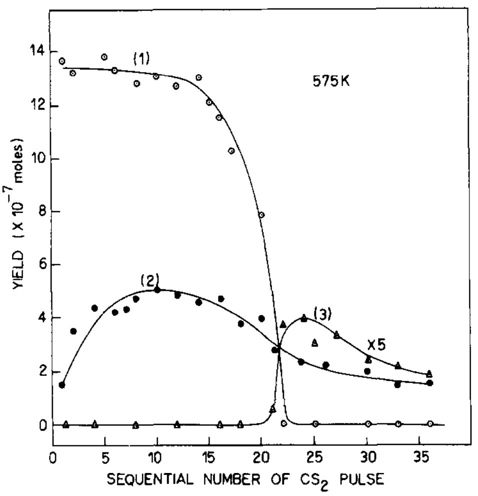

FIG. 1. CH_4 yields from successive pulses of CO (1.6 μmole) and CS_2 (1.4 μmole) injected alternately over Ru/alumina catalyst at 575 K in the presence of H_2 carrier gas. Curve 1—CH_4 from CO; curve 2—CH_4 from CS_2; curve 3—CO from CS_2 pulse injections (yield amplified five times).

ucts CO and H_2S in addition to CH_4. The CO yields as a function of number of CS_2 pulses are shown by curve 3 of Fig. 1. The H_2S gas chromatograms were found to be heavily tailing at the initial stages and were difficult to measure quantitatively. The maximum yields of CH_4 (from active catalyst) and those of CO and H_2S (from poisoned catalyst) observed per CS_2 pulse injection at different catalyst temperatures are given in Table 1. The mass spectra recorded on injection of CS_2 over poisoned (for CO methanation) catalyst contained a large number of small unidentified peaks in the mass range 35–70 which were not observed from active catalyst.

While no elution of unreacted CS_2 was detected at catalyst temperatures above 525 K, even after 75 pulse injections of CS_2, at 475 and 500 K CS_2 breakthrough was observed after 15 and 30 pulse injections, respectively. CS_2 amounts released after 50 injections were about 8 and 5% per pulse at 475 and 500 K, respectively.

(B) *Reaction of CS_2 on Catalyst Surface in Presence of He Carrier Gas*

(a) Injections of CS_2 pulses over freshly regenerated catalyst in a He carrier flow produced CO_2 and the yields of CO_2 depended on catalyst temperature. After the initial burst release of CO_2 as mentioned above, the effluent gas was periodically sampled and analysed. Though no release of CS_2 was observed, CO_2 was found to be continuously released at a slow rate, the release rate being less at lower temperatures. Thus, small quantities of CO_2 continued to be released for 30 min at 529 K and it was complete in 5 min at 625 K. Also, no release of unreacted CS_2 was observed when a CS_2 pulse was injected at a lower temperature (<500 K) and the temperature was subsequently raised to 650 K.

Repeat injections of CS_2 showed an increase in the yield of CO_2 and the formation

TABLE 1

Maximum Yields of CH_4 (from Active Catalyst) and Those of CO and H_2S (from Poisoned Catalyst) Observed on Injection of a CS_2 Pulse (1.4×10^{-6} moles of CS_2) into a H_2 Stream Flowing through a Catalyst

Catalyst temperature (K)	1 CH_4 ($\times 10^{-7}$ mole) ($\pm$ 0.5)	2 CO ($\times 10^{-7}$ mole) ($\pm$ 0.2)	3 H_2S ($\times 10^{-7}$ mole) ($\pm$ 1.0)
525	2.6	0	7.4
550	4.2	0.4	9.0
575	4.8	0.8	11.5
600	5.4	1.4	7.9
625	6.1	1.7	6.0
675	7.0	2.0	Not measurable

TABLE 2

Initial and Maximum Yields of CO and CO_2 Observed from Successive Pulse Injections of CS_2 1.4 × 10^{-6} moles) on Ru/Alumina and γ-Alumina in the Presence of He Carrier Gas

Catalyst temperature (K)	(A) Ru/alumina (× 10^{-7} mole)			(B) γ-alumina (× 10^{-7} mole)			
	CO_2 initial value (± 0.1)	CO_2 maximum yield (± 0.1)	CO maximum yield (± 0.05)	CO		CO_2	
				Initial value (± 0.05)	Maximum yield (± 0.05)	Initial value (± 0.05)	Maximum yield (± 0.1)
525	0	2.8	0.3	0	0.12	Not measurable	2.8
575	Not measurable	4.2	1.0	0.1	0.4	0.9	3.2
600	—	—	—	0.16	0.9	1.5	3.8
625	2.5	6.8	1.3	0.2	1.2	3.6	6.2
675	2.8	6.0	1.6	0.3	1.8	7.4	5.8

of CO in addition to CO_2 was observed at all temperatures above 500 K. The yields of both CO_2 and CO attained near-saturation values on successive CS_2 pulse injections. The initial and saturation yields of CO_2 and CO thus observed are given in Table 2A and the typical variation in their yields with the sequential number of the CS_2 pulse is shown by curves 1 and 2 of Fig. 2 for a catalyst temperature of 575 K.

Mass spectral studies under similar conditions showed that in addition to CO_2 and CO as mentioned above, a small amount of unreacted CS_2 was eluted along with new products COS, SO_2, and H_2S. The variation in yields of these products as a function of the sequential number of the CS_2 pulse is shown in Fig. 3. It may be noted that the number of CS_2 pulse injections after which sulphur products were formed increased significantly with catalyst temperature. Thus at 474 K, the breakthrough of CS_2 and the formation of sulphur compounds were observed after the 14th pulse injection, the corresponding numbers at 550 and 625 K being 25 and 53, respectively. The maximum extent to which unreacted CS_2 eluted was 15, 3, and 0.5% at 475, 500 and 625 K, respectively, as observed for the 70th pulse injection of CS_2. No slow release of adsorbed CS_2 was observed when the effluent gases were further analysed after initial release of unreacted CS_2 at different catalyst temperatures.

(b) To evaluate the H_2 reactivity of species formed on the catalyst surface in its interaction with CS_2, following a CS_2 pulse injection into He carrier gas, 10 successive injections of 2 ml H_2 were made and the

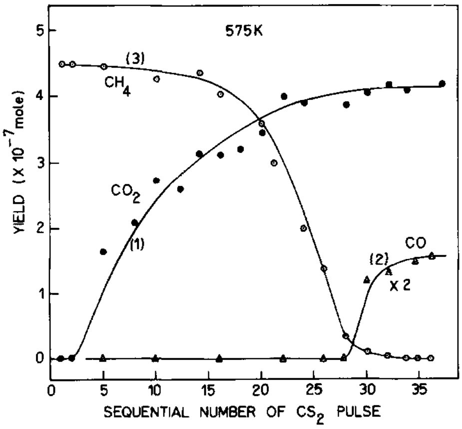

FIG. 2. Variation in yields of CO_2 (curve 1) and CO (curve 2, yield amplified two times) per CS_2 pulse on successive injection of CS_2 (1.4 μmole) on Ru/alumina at 575 K in the presence of He carrier gas. Curve 3 shows the total CH_4 yield obtained on 10 successive H_2 injections following a pulse of CS_2, the time gap between CS_2 and first H_2 injection being 1 min.

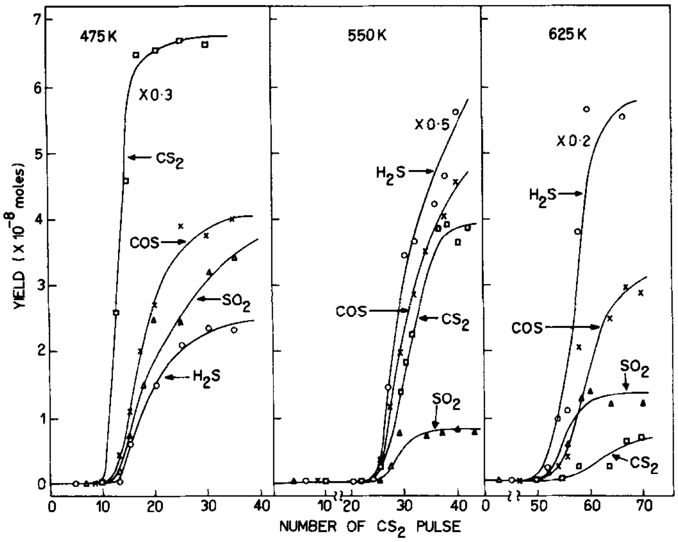

FIG. 3. Variation in yields of sulphur compounds as a function of the sequential number of the CS_2 pulse injected in the presence of He carrier gas.

reaction products were analysed at each stage.

(i) When a CS_2 pulse was followed by a H_2 injection (referred to as "first H_2" in the succeeding text), formation of methane was observed. Further H_2 injections at intervals of 2 min gave decreasing yields of CH_4, the extent of the decrease being dependent on the catalyst temperature. The time elapsed between the CS_2 and the first H_2 injections had considerable influence on methane yields. Typical examples of methane yields obtained on successive H_2 injections for different CS_2-first H_2 time gaps and for different catalyst temperatures are given in Figs. 4A–F.

It may be noted that at 450 K the CH_4 yield from the first H_2 pulse increases initially up to a CS_2-first H_2 time gap of 5 min and then decreases. At 475 K the corresponding time is 10 sec and at higher temperatures it decreases progressively for all time gaps studied. Similarly, a progressive variation of total methane yield (sum of CH_4 from successive H_2 pulses as indicated by the total heights of vertical plots in Fig. 4) with catalyst temperature may be noted. At 450 K, the total CH_4 yield increases for time gaps up to 20 min. At 475 K it is almost constant and at temperatures higher than 475 K it decreases with increasing CS_2-first H_2 time gap.

(ii) When CS_2 and H_2 were injected simultaneously the CO_2 yields were less than those given in Table 2A.

(iii) When the sequence of CS_2 and H_2 injections as in (i) was repeated at a particular catalyst temperature, the CH_4 yields progressively decreased. The typical variation of CH_4 (total) yield at 575 K as a function of number of CS_2 pulse injections is shown by curve 3 of Fig. 2 for comparative evaluation of the data.

(iv) After complete poisoning of the catalyst (i.e., when injection of H_2 following a CS_2 pulse gave no CH_4), the H_2 injection subsequent to that of a CS_2 pulse gave rise to H_2S formation. Further H_2 injections again gave decreasing amounts of H_2S and the H_2S yields further decreased with increase in the CS_2-first H_2 injection time gap. The effect of the CS_2-first H_2 time gap on the total H_2S yield (obtained on adding up H_2S from four successive H_2 injections following a pulse of CS_2) is shown in Fig. 5. It may be noted from this figure that with increase in catalyst temperature the H_2S yield first increases and at

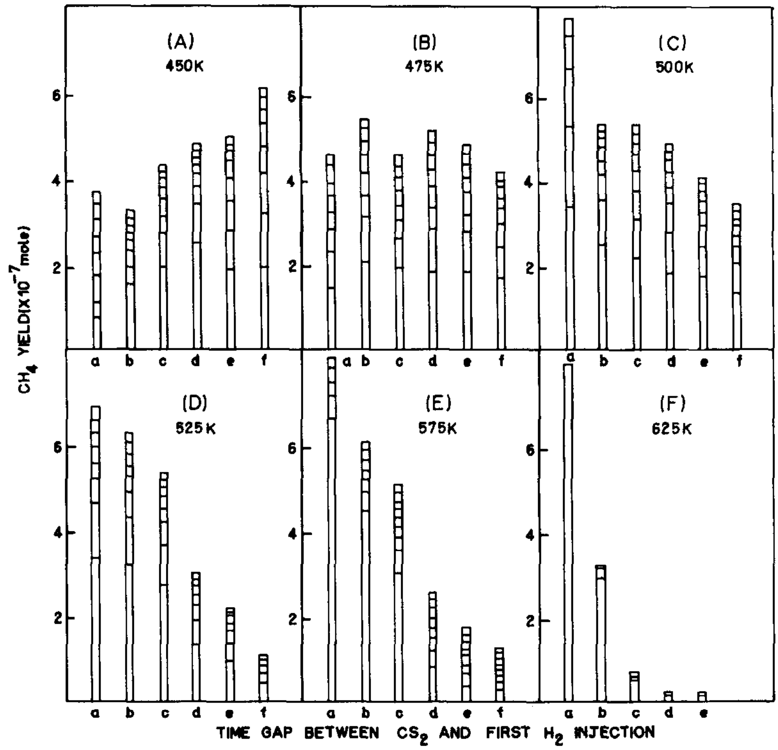

FIG. 4. Methane yields obtained at different temperatures on injection of a 200-μl pulse of CS_2 vapour/He (1.4 μmole CS_2) followed at different time gaps by successive injections of 2 ml H_2. Horizontal lines in these figures indicate the methane yields obtained for each of the successive H_2 injections. Thus, the distance between the abscissa axis and the first line indicates the CH_4 yield for the first H_2 injection, between first and second lines for the second H_2 injection and so on. (a) to (f) refer to the time interval between a CS_2 pulse and first H_2 injection. a—0 (simultaneous CS_2 and H_2), b—10 sec, c—1 min, d—5 min, e—10 min, and f—20 min.

temperatures greater than 575 K a sharp decrease in H_2S yield is observed. Also, the curves in Fig. 5 can be resolved into at least two components, one being fast and the other slow.

(C) Reaction of CS_2 on γ-Alumina

To evaluate the role of support material in the interaction of CS_2 on Ru/alumina catalyst, the experiments as in Sections 3A and B were repeated using the metal-free γ-alumina (the support material used for the preparation of the catalyst). The samples were pretreated in H_2/He as was done for the Ru/alumina samples.

(i) When CS_2 vapour was injected into H_2 carrier gas flowing through γ-alumina, no CH_4 was formed at all temperatures up to 675 K (cf. Section 3A). After 15–20 successive CS_2 injections the formation of CO and H_2S was observed. The H_2S yields were much lower than those given in Table 1 and the gc peaks were heavily tailing and nonreproducible.

(ii) Injection of CS_2 pulses in the He carrier gas flowing through alumina at different temperatures gave rise to CO and CO_2 formation. On further injections of CS_2, the yield of CO increased progressively, while that of CO_2 first increased and then gradually decreased. The initial and maximum yields of CO and CO_2 at different temperatures are shown in Table 2B. After about 30 injections of CS_2 pulses small peaks due to H_2S were noticed though

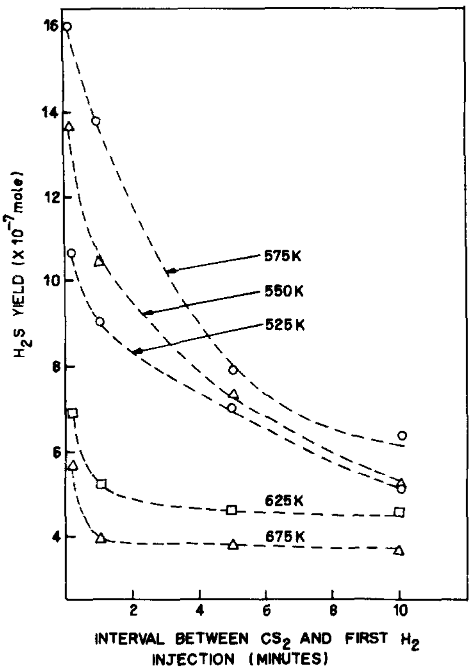

FIG. 5. Total H_2S yields from four H_2 injections following a pulse of 200 μl CS_2/He (1.4 μmole CS_2) as a function of time interval between CS_2 and first H_2 injection.

their exact amount was not measured due to heavy tailing in the gc peaks.

(iii) To evaluate the role of surface-adsorbed O_2 or H_2, the metal-free alumina was heated under vacuum ($\sim 10^{-3}$ Torr) at 850 K for 30 min and then at 625 K for 4 hr. CS_2 vapour was allowed to interact with the catalyst at 625 K under vacuum. The reaction products analysed by mass spectrometry contained CO, CO_2, COS, SO_2, and H_2S along with some unidentified species.

(D) XPS Studies

Figure 6 shows the XPS spectrum of a fresh catalyst sample and that of a sample exposed at 575 K for 10 min to a continuous flow of CS_2/He. It is evident that exposure of the catalyst to CS_2 results in the formation of carbon and sulphur. The binding energy (B.E.) of S $2p$ and S $2s$ peaks were found to be 163.5 and 227.2 eV, respectively, as calculated from high-resolution XPS sepectra. Though the C $1s$ signal merges with the Ru $3d_{3/2}$ peak at 284.1 eV, the ratio of the two Ru peaks at 280 and 284.1 eV in spectra (a) and (b) clearly indicates the formation of carbon on the catalyst exposed to CS_2 vapour. The B.E. values of the carbon and sulphur signals observed in these experiments are close to the values of these species in their elemental form (*11*).

In order to establish the spatial distribution of Ru and S on the pellet surface and to see whether S coverage occurs predominantly over Ru sites, line-scan Auger spectra were recorded. Preliminary results indicated that considerable S coverage occurred over Ru sites.

4. DISCUSSION

It is as yet too involved to analyse and suggest exact mechanistic routes for the formation of the various products reported here. However, certain specific trends can be discussed here.

The important observations which require explanation are the formation of H_2S and oxides of carbon and sulphur in the experiments under inert atmosphere or under vacuum (Sections 3B, C) since free hydrogen and oxygen were not available in these studies. The only conclusion one can draw is that the acidic OH groups on the alumina are the source of oxygen and hydrogen. Hydroxyl groups are known to be present on alumina at temperatures as high as 1100 K even under vacuum (*12, 13*). X-Ray analysis of the catalysts used in this study confirmed the presence of hydroxyl groups. The work of Foger and Anderson (*14*) wherein CO oxidation was observed on clean alumina and metal/alumina surfaces in the absence of oxygen tends to support our suggestion.

The possible routes of formation of CH_4 and H_2S in the experiments reported here are the following: (i) The CS_2 may remain adsorbed on the catalyst surface and react directly with H_2. (ii) CS_2 may decompose to give elemental carbon and sulphur and

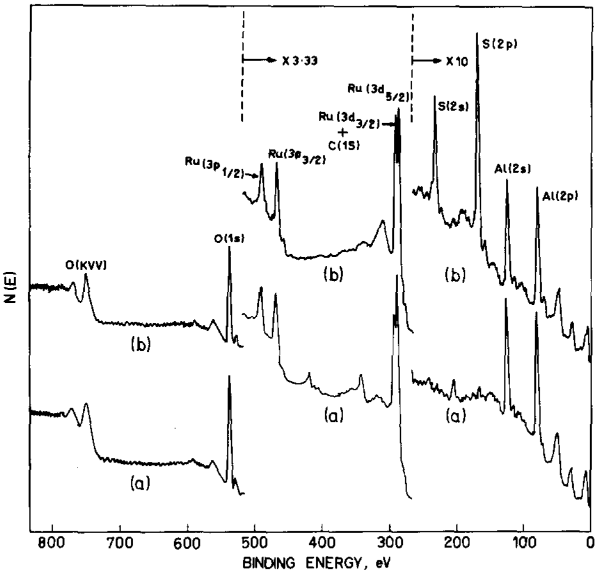

FIG. 6. XPS spectra of (a) fresh Ru/alumina catalyst and (b) catalyst exposed to CS_2 vapour at 575 K under He stream.

these in turn react with H_2 to give hydrocarbons and H_2S, respectively.

If the formation of CH_4 and H_2S is via the first route, then the decrease in their yields with the CS_2–H_2 injection time gap as shown in Figs. 4 and 5 can be expected only if adsorbed CS_2 on the catalyst surface is released slowly leaving smaller amounts of adsorbed CS_2 with time. However, the results show that, for the number of CS_2 pulses injected in our experiments, slow release of unreacted CS_2 was absent at all temperatures up to 650 K.

Data in Fig. 6 clearly show that CS_2 decomposes on the catalyst surface, even under an inert atmosphere, to give elemental carbon and sulphur. Decomposition of CS_2 to C and S on Fe catalysts has been reported in the literature (*15*). Similar decomposition of H_2S accompanied by deposition of S and elution of H_2 has been reported by various workers under different experimental conditions (*6*, *7*, *16–18*). The work of Ng and Martin (*7*) has confirmed that S formed on decomposition of H_2S on Ni/SiO_2 is in elemental form and no Ni bulk sulphides are formed. Also, higher coverages result in S-cluster formation.

The higher yields of CH_4 and the lower yields of CO_2 observed on simultaneous injections of CS_2 and H_2 (see Fig. 4 and also Section 3B) indicate that CO and CO_2 eventually become methanated. The mechanism of CO and CO_2 methanation on Ru catalysts has been discussed in an earlier article (*9*). It has been shown that the methanation of both the CO and CO_2 occurs via "active" carbon formation and the carbon loses its activity towards H_2 with increasing temperature and time. The formation of CH_4 on injection of CS_2 and H_2 in the presence of He carrier gas (Fig. 4) has an apparent parallelism with the formation of CH_4 in the CO_2–H_2 reaction on Ru catalyst (*9*). Apparently, the slow desorption of CO_2 and the loss in the activity of carbon (formed from CS_2 or CO_2) are responsible for the variation in methane yield with CS_2–H_2 time interval as shown in Fig. 4.

The formation of C_2–C_4 hydrocarbons in the CS_2–H_2 reaction (Section 3A) indicates that higher hydrocarbons from C_1 species are formed via nonoxygenated complexes. This result is in agreement with recent studies on the Fischer–Tropsch synthesis (*19–23*) wherein it has been shown that surface carbon–hydrogen species such as $M = CH_2$ are first formed and these polymerise to give higher hydrocarbons. However, formation of higher hydrocarbons through the participation of nonoxygenated complexes can be unequivocally proved only if the CS_2 interaction with H_2 over clean single crystals of Ru is studied.

Since no measurable CH_4 formation was observed in the CS_2–H_2 reaction on metal-free γ-alumina (Section 3C) it is clear that the C or CO_2 available on Ru sites only is methanated. The data of Fig. 2 thus clearly indicate that successive injection of CS_2 causes the blocking of Ru sites, thus resulting in reduced amounts of CO or CO_2 held on the catalyst and hence reduced CH_4 yields. The Auger line-scan data tend to support this conclusion. These observations are in agreement with the work of Ng and Martin (*7*) and that of Fischer and Kelemen (*6*) who observed decreasing adsorption of different gases, e.g., CO, H_2 on Ni and Ru, with increasing S coverage from H_2S. Furthermore, the formation of CH_4 from CS_2 even after the catalyst was poisoned for CO methanation (Fig. 1) clearly indicates the existence of at least two types of Ru centres where CO and CS_2 undergo decomposition.

The formation of sulphur compounds only at the stage of CS_2 breakthrough (Fig. 3) which also coincides with the catalyst poisoning for CH_4 formation is an interesting aspect to be noted. Such a behaviour could be expected if (a) there are two different types of centres where CS_2 could be chemisorbed and initially CS_2 is selectively chemisorbed at one type of centre. One of these centres could be Ru atoms themselves with the other one in the host material adjacent to OH groups; (b) sulphur in a weakly held second adsorbed overlayer only reacts with H_2 rather than in the strongly held chemisorbed layer.

The effect of the time delay between CS_2 and H_2 pulse injections as shown in Fig. 5 suggests that the activity of "nascent" sulphur towards H_2 also decreases with temperature and time similar to that of carbon (*9*). The faster decay in sulphur activity at higher temperatures could thus explain the lower H_2S yields at temperatures greater than 575 K as shown in Table 1 and Fig. 5. Some of these aspects are under detailed evaluation.

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