Petroleum Res. J. Vol. 11 (1999); P. 51-59, 9 Figs.

35S-Radiotracer Studies of Sulphur Poisoning of Platinum Supported Catalysts: 2. Hydrogenation of Ethyne

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دراسة سمومية الكبريت – 35s لحفازات البلاتين المدعم على السيليكا والألومنيا وتتبعها بالتقفى بالأثر الأشعاعي: 2 – هدرجة الإيثين

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تم دراسة سمومية الكبريت لحفازات البلاتين المدعم على السيليكا (Europt-1) 6% Pt/SiO2 والألومينا (Europt-3) 0.3% Pt/Al_2O_3، لامتزاز أول أكسيد الكربون (CO) والمواد الهيدروكربونية، الإيثاين (C_2H_2) والإيثين (C_2H_4) وتفاعل الإيثين مع الهيدروجين (C_2H_2/H_2) باستخدام ظاهرة التقفى بالأثر الأشعاعي وباستعمال كبريتيد الهيدروجين المرقم بعنصر الكبريت المشع (35_S-H_2S) والكربون –14 بنظام مغلق عند درجة 293±2K.

سلوك إمتزاز 35_S-H_2S تم على مرحلتين، بالمرحلة الأولى كان الامتزاز كبيراً وسريعاً وبالمرحلة الثانية بيّن خط للتشبع كدليل لتكوّن طبقة أولية من كبريتيد الهيدروجين الممتز. نسبة 5% فقط من كبريتيد الهيدروجين الممتز يمكن أزالتها بالتفريغ. من خلال النتائج فقط اقترح بأنه عند ضغوط عالية من كبريتيد الهيدروجين $H_2S>2.5$ ، هذه الحفازات تمر بعملية إعادة بناء لسطحها وأن امتزاز الكبريت يرغم أول أكسيد الكربون والإيثين للامتزاز على المواقع الحامضية الموجودة على Al_2O_3.

من خلال النتائج لوحظ أنه، كلما زادت درجة التسمم بعنصر الكبريت فإن انتقائية النواتج تزداد على الحفازات المدعمة على الألومينا بينما وجد العكس على الحفازات المدعمة على السيليكا وأن آلية تسميم الكبريت لهذه الحفازات هي غلق للمواقع التي يتم عليها إمتزاز المواد الهيدروكربونية وهدرجتها.

مجمل النتائج بيّنت أن إنتقائية المنتوجات بتفاعل الإيثاين على هذه الحفازات، تحت الظروف الاعتيادية وظروف التسمم بالكبريت، محكومة بعامل حركي حراري مما يعزز مقترحاتنا السابقة بأنه تحت ظروف امتزاز وهدرجة المواد الهيدروكربونية فإن هذه الحفازات تمر بعملية إعادة بناء لسطحها.

Abstract: *The sulphur deactivation of 6 % Pt/SiO_2 (Europt–1) and 0.3% Pt/Al_2O_3 (Europt–3) catalysts for carbon monoxide, ethene and ethyne adsorption and ethyne hydrogenation has been investigated, using sulphur labelled hydrogen sulphide, ^{35}S-H_2S and 14C-radiotracer of the corresponding adsorbate at 293±2K. Adsorption of ^{35}S-H_2S occurs in two stages. On Europt-1, it showed a non-linear primary region followed by a linear secondary region, while on Europt-3, it showed a linear primary region followed by a plateau region. A small fraction ca. 5% of the adsorbed sulphur species can be removed by evacuation. It is suggested that at high sulphur coverages, $H_2S < 0.5$, these catalysts surfaces undergo some reconstruction.*

It was observed that the effect of sulphur poisoning on the selectivity for ethene formation was beneficial for the alumina-supported catalysts

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whilst detrimental to the silica-supported catalysts. Furthermore, sulphur promotes carbon monoxide and ethene adsorption on the Al_2O_3 *acidic sites. In addition, it appears that the poisoning behavior of sulphur on the hydrocarbons adsorption and ethyne hydrogenation on these catalysts is simply due to a hydrocarbon site-blocking effect.*

Evidence has been obtained to support our previous proposals that, on steady state catalysts and under the influence of hydrocarbon adsorption and ethyne hydrogenation reactions a surface reconstruction process occurs and ethyne hydrogenation takes place in the secondary adsorption region. Collectively, the results indicate that Europt-1 and Europt-3 catalysts under clean and sulphur poisoning conditions exhibited a high thermodynamic selectivity but low mechanistic selectivity towards ethyne hydrogenation reaction.

INTRODUCTION

The phenomenon of catalyst poisoning is one of the most serious problems associated with the industrial applications of supported metal catalysts in numerous catalytic reactions, especially those involving hydrogen, such as, methanation of coal and its conversion to fuels and chemicals, reforming of naphtha or hydrocarbon hydrogenations. The extremely harsh poisoning encountered in these catalytic systems is that induced by sulphur, mainly because of the fact that the feed stock of these reactions usually contains significant amounts of sulphur containing compounds, such as, H_2S, COS, SO_2, CS_2, or organic sulphides. Sulphur apparently bonds so strongly to metal surfaces and a marked reduction in the catalyst activity may occur even at extremely low concentrations (PPb quantities). Hence, the life of the catalyst may be reduced and its regeneration process is impossible or impractical[1]. On the other hand, the chemisorption of sulphur on metal catalysts may cause beneficial effects on the selectivity by partial and well controlled poisoning. The topic of sulphur poisoning of metallic catalysts has been reviewed comprehensively by many investigators[1-3].

From our previous results[4,5] on ethyne hydrogenation on the same stock of these catalysts, it was apparent that these catalysts possessed poor selectivities (~ 0.30–0.6) for the production of mono-olefins from di-unsaturated hydrocarbons. The objectives of the present studies were a detailed investigation of the effects of the presence of sulphur upon the adsorption characteristics of carbon monoxide (CO), ethyne (C_2H_2) and ethene (C_2H_4) and on the selectivities of ethyne hydrogenation (C_2H_2/H_2) processes on the same platinum catalysts.

EXPERIMENTAL

Apparatus

The apparatus which was used in this work consisted of a conventional vacuum system which was maintained at a pressure of ~0.01 Pascal (Pa) by using a mercury diffusion pump backed by an oil rotary pump. The system contained a series of bulbs for the storage of non-radioactive and radioactive gases and a reaction vessel where the adsorption of ^{14}C-labelled hydrocarbons, the reaction of ethyne with hydrogen and the ^{35}S-sulphur poisoning experiments were carried out (Fig. 1).

Catalysts

The catalysts employed in this study are standard reference catalysts designed by the Council of Europe Catalysis Group (EUROCAT). Europt–1, is a 6% (w/w) Pt/SiO_2 catalyst with a total surface area of 185 $m^2\,g^{-1}$ and a pore volume of 0.72 $cm^3\,g^{-1}$, prepared by Johnson Matthey Chemicals plc [6]. Europt^{-3}, is a 0.3% (w/w) Pt/Al_2O_3–0.82 % Cl catalyst and is being used

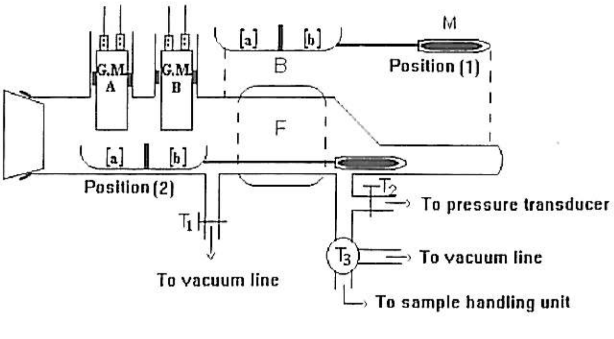


Fig. 1. Reaction vessel used for direct monitoring of surface adsorbed-species. (G.M, Geiger-Muller counters; F, furnace region; B, catalyst boat, position (1) for catalyst reduction and position (2) for surface monitoring; M, glass magnet; $T_{1,2,3}$, glass stopcocks.

commercially under the code KETJEN-CK 303 with a surface area of 184 m^2 g^{-1} and a pore volume of 0.49 cm^3 g^{-1} [7].

Another two platinum catalysts supported on silica (Cab-O-Sil) and γ-alumina (Degusa Ltd.) were prepared at Glasgow University[8] by the impregnation method and characterised as, (w/w), 0.8% Pt/SiO$_2$ and 0.8% Pt/Al$_2$O$_3$. They were used in this study for comparison of the results of variation of selectivity with extent of sulphur poisoning with those obtained on the EUROPT-catalysts.

Materials

Hydrogen gas (B.O.C., Commercial grade) was used in the catalysts reduction and hydrogenation reactions without further purification. The non radioactive hydrocarbons, C_2H_2, C_2H_4 and C_2H_6 (Air Products Ltd.) were degassed at liquid nitrogen temperature (77 K) for ~ 15 minutes followed by bulb-to-bulb distillation using liquid nitrogen and methylene chloride + solid CO$_2$ mixture. Helium, methane and carbon monoxide (Air Products Ltd.) were used as supplied. The ^{14}C-radioactive hydrocarbons, $^{14}C_2H_2$ and $^{14}C_2H_4$ were purchased from the Radiochemical Centre, Amersham, U.K. and diluted with the corresponding non-radioactive gas to give a count rate of about 25 counts min^{-1} Pa^{-1}. ^{14}CO was prepared by the reduction of $^{14}CO_2$ using metallic zinc as described elsewhere[9]. ^{35}S-hydrogen sulphide was supplied by Sigma Radiochemicals and diluted with the non-radioactive H$_2$S to produce a count rate in the range of 20–25 counts min^{-1} Pa^{-1}.

Procedure

The procedures employed in the reduction of catalysts, adsorption of ^{14}C-hydrocarbons and ethyne hydrogenation reactions have been described previously[5]. In the ^{35}S-hydrogen sulphide poisoning experiments, catalysts in a finely grinded form (typically 0.30 0.05g, 100 B.S.S. mesh) were reduced in flowing H2 (30 cm^3 min^{-1}) at 523K for 2 h and then cooled *in vacuo* to room temperature (*ca.*293±2K). When ^{14}C-hydrocarbons, ^{14}CO adsorptions or C_2H_2/H_2 hydrogenation experiments were required, an aliquot of 0–0.5 Kpa (1Kpa = 1000 pa) of ^{35}S-H$_2$S was admitted into the reaction vessel, and kept in contact with the catalyst for 15 minutes. The radioactivity content was counted, the reaction vessel was then evacuated for 15 minutes to remove any gas phase ^{35}S-H$_2$S and three successive count rates, which represent the sulphur-uptake by the catalyst were recorded. The adsorptions of ^{14}C-hydrocarbons and ethyne hydrogenation were then performed as described[5].

RESULTS AND DISCUSSION

Adsorption of ^{35}S-H$_2$S

Samples of Europt-1 and Europt-3 were reduced with hydrogen and activated as described above. Controlled aliquots of ^{35}S-H$_2$S were admitted to the reaction vessel and the surface and gas phase count rates were determined after each addition. Figure 2 presents the adsorption isotherms produced. The isotherms showed a pattern similar to that reported for ^{14}C-hydrocarbons on these catalysts[4,5]. These showed two distinct regions, a steep primary region followed by a linear secondary region. The secondary region of the isotherms (in particular on Europt-1)) rose linearly with increasing gas pressure. This behavior is in accordance with the results of kinetic studies[10] of the rate of sulphur adsorption on Pt-catalysts which revealed that H$_2$S adsorption was very rapid at low sulphur coverages (H$_2$S = 0.25–0.3) while at H$_2$S > 0.3, sulphur adsorbed slowly. It has been suggested this may be due to the decrease in the sticking coefficient.

On Europt-1, *ca.* 5% of the total amount of the ^{35}S-adsorbed species was removed by evacuation for 30 minutes. Hydrogen sulphide has been reported[11,12] to adsorb dissociatively as one sulphur atom strongly bonded to two Pt atoms or one sulphur atom weakly bonded to one Pt atom at similar experimental conditions. This observation proposes that sulphur is adsorbed on the metal surface and an indication that the adsorption process is partially reversible with the removable proportion likely to belong to the weakly bonded sulphur species.

Admission of further aliquots of ^{35}S-H$_2$S to the catalyst (Europt-1) resulted in a continuous build-up of the sulphur species on the catalysts until a

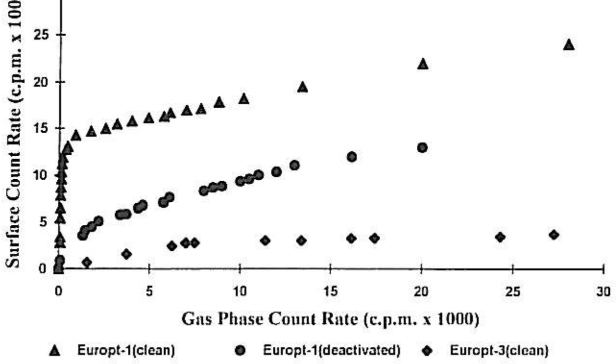


Fig. 2. Adsorption of ^{35}S-H_2S on Europt-1 and Europt-3 at 293±2K.

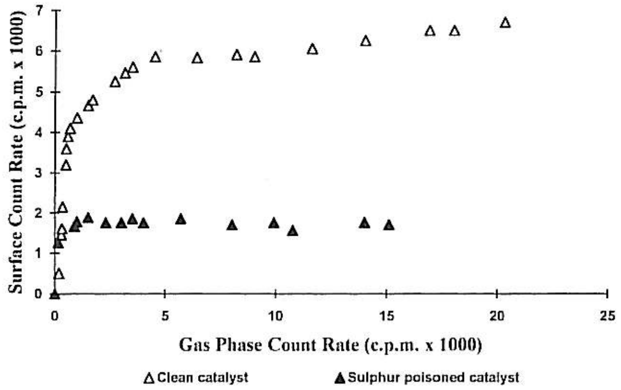


Fig. 3. Adsorption of ^{14}C-ethyne on clean- and sulphur-poisoned Europt-1 at 293±2K.

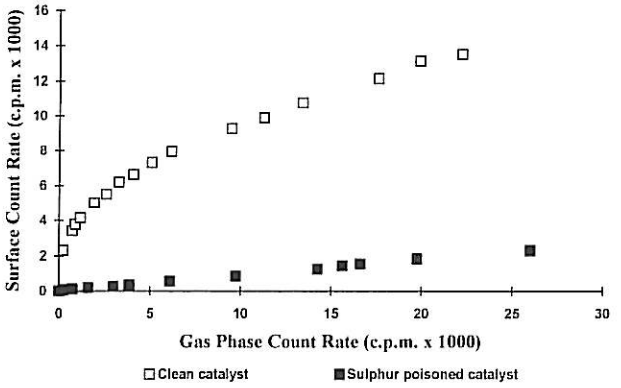


Fig. 4. Adsorption of ^{14}C-ethyne on clean- and sulphur-poisoned Europt-3 at 293±2K.

plateau region was reached (at *ca.* 30 Kpa per gram catalyst). The saturation value was then taken as to correspond to the completion of monolayer coverage and used to calculate sulphur coverage (H_2S) in the subsequent poisoning experiments.

When ^{35}S-H_2S adsorption on steady state catalysts (catalysts deactivated with C_2H_2/H_2 reactions) was investigated, the extent of sulphur adsorption on the primary region was substantially reduced. Although the amount adsorbed in the secondary region was less than that adsorbed on clean catalysts, the isotherms had similar gradients. This suggests that some of the sites in the primary adsorption region, possibly for geometric reasons, can not accommodate hydrocarbon species and were available for sulphur adsorption and that these sites are responsible for the adsorption-activation of hydrogen in ethyne hydrogenation.

Adsorption of ^{14}C-ethyne on poisoned catalysts

A number of ^{14}C-ethyne adsorption isotherms have been determined as described above on clean catalysts and catalysts being poisoned with an amount of ^{35}S-H_2S corresponds to $H_2S = 0.25$, under identical conditions. The results obtained on Europt-1 and Europt-3 are shown in figures 3 and 4 respectively. As it can be seen, pre-adsorption of sulphur on the catalysts surfaces considerably suppressed the amounts of ^{14}C-ethyne that could be adsorbed compared with those adsorbed on sulphur-free surfaces. This effect was remarkably pronounced in the secondary adsorption region which showed a plateau behavior as the pressure of adsorbates was increased. Since the hydrocarbon species undergoing hydrogenation as reported[4,5,9] are located in this region, the latter behaviour tempts to conclude that the poisoning effects of sulphur is due simply to hydrocarbon site-blocking effect.

On Europt-1, evacuation of the catalysts for 30 minutes, resulted in the removal of ca. 20% of the hydrocarbon species adsorbed in this region. Admission of ^{14}C-ethyne on to catalysts with high sulphur coverages, $H_2S > 0.25$, resulted in continuous drop in the surface radioactivity, presumably as a consequence of an interaction between the adsorbed sulphur species and ethyne molecules, leading to the formation of unidentified sulphur containing carbonaceous species. These results also provide evidence to suggest that a surface reconstruction process takes place as a result of sulphur adsorption, thus limiting the extent of C_2H_2 adsorption to the exposed metal sites left vacant, probably as electron deficient sites. They also provide evidence to support the suggestion made previously[4,5] that the turning point of the hydrocarbon adsorption isotherms corresponds to a surface reconstruction process involving the migration of the metal atoms, left vacant at the surface after completion of the primary adsorption process. These form an array with the hydrocarbonaceous residues, thus enhancing the hydrocarbon adsorption as a secondary adsorption process which takes place on these modified sites.

On Europt-3, it is likely that sulphur has completely poisoned the metallic sites of this catalyst, whilst, at the same time promoting some adsorption of hydrocarbons on the support material (Al_2O_3).

Adsorption of ^{14}C-ethene on Poisoned Catalysts

In a series of adsorption experiments on H_2S poisoned catalysts, samples of the catalysts under investigation were reduced and poisoned with ^{35}S-H_2S in the described manner. This was followed by measuring the ^{14}C-ethene adsorption isotherms. Figures 5 and 6 show the isotherms obtained on Europt-1 and Europt-3 respectively. On Europt-1, striking features emerged at varied sulphur coverages. At $H_2S = 0.25$, the adsorptive capacity of $^{14}C_2H_4$ in the primary and secondary regions were enhanced. At $H_2S = 0.35–0.5$, the adsorption of $^{14}C_2H_4$ in the secondary region was remarkably reduced showing a plateau behavior, while the position of the turning point remained unchanged. At H_2S 0.5, and as noticed in the $^{14}C_2H_2$ adsorptions, a continuous drop in the surface count rate was observed, suggesting the occurrence of an interaction between the pre-adsorbed sulphur and the $^{14}C_2H_4$ molecules, forming some sulphided carbonaceous species. Evacuation of the reaction vessel for 30 minutes after the build-up of the ^{14}C-C_2H_4 isotherms resulted in a decrease in the surface count rate to a value corresponding to the turning point of the adsorption isotherms.

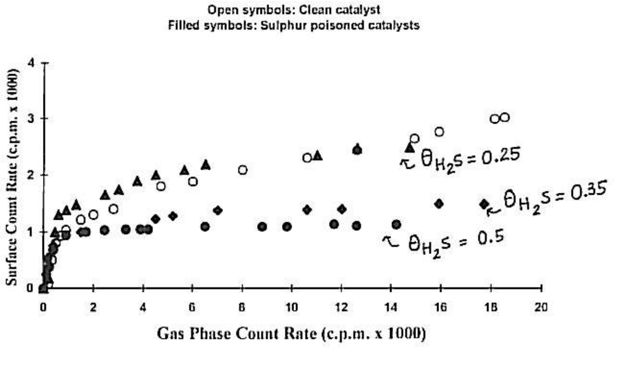


Fig. 5. Adsorption of ^{14}C-ethene on clean- and sulphur-poisoned Europt-1 at 293±2K.

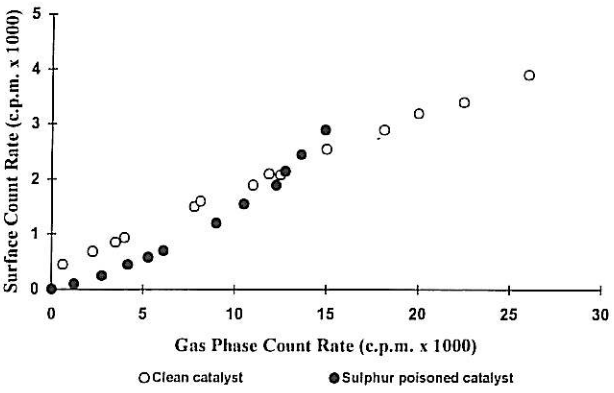


Fig. 6. Adsorption of ^{14}C-ethene on clean- and sulphur-poisoned Europt-3 at 293±2K.

On Europt-3, at $H_2S = 0.25$, sulphur completely suppressed the adsorption of $^{14}C_2H_4$ in the primary region, whereas an enhanced uptake of ethene was observed to occur as the pressure of $^{14}C_2H_4$ was increased, showing an up-ward concave curve which is a characteristic of a physical adsorption process[13].

It is important to note that, on the catalysts under study, the extent of sulphur-induced suppression of the hydrocarbon adsorption capacity was less with ethene than with ethyne.

Adsorption of 14C-Carbon Monoxide on Poisoned Catalysts

Carbon monoxide adsorption has been widely used as a probe for catalyst surface area determination and to distinguish the active centres in the catalytic reactions[9,13,18,19]. In order to gain an insight to the fate of such centres as a result of sulphur poisoning in the ethyne hydrogenation reaction on platinum catalysts the adsorption of ^{14}CO on these catalysts has been examined. Controlled pulses of ^{35}S-H_2S were admitted to the freshly reduced catalysts as described above to give a sulphur coverage of $H_2S = 0.25$. ^{14}C-carbon monoxide adsorption isotherms were obtained by admitting successive aliquots of ^{14}CO to the S-poisoned catalysts. These isotherms are shown in figure 7 (for Europt-1) and figure 8 (for Europt-3). The isotherms show interesting and important differences between the adsorption of ^{14}CO on freshly reduced and S-poisoned catalysts. On (Europt-1), at low sulphur coverages, H_2S 0.5, the isotherms showed similar shapes to that observed on the clean catalyst, in the sense that the adsorption continued to increase as further ^{14}CO was admitted to the reaction vessel. At H_2S 0.5, the ^{14}CO showed different behavior. The surface count rate rose rapidly with increased gas pressure to a saturation value, then remained constant as the ^{14}CO pressure was increased (Langmuir type isotherm). These results are consistent with the suggestion made above, that in the presence of sulphur, a surface reconstruction process takes place on the catalyst. Such a phenomenon has also been proposed on surfaces of single crystals[14].

Evacuation of the reaction vessel for 30 minutes resulted in the removal of *ca.*10% of the adsorbed ^{14}CO species. According to an IR study[15] such removable species may be assigned to weakly adsorbed CO on sulphur-poisoned sites.

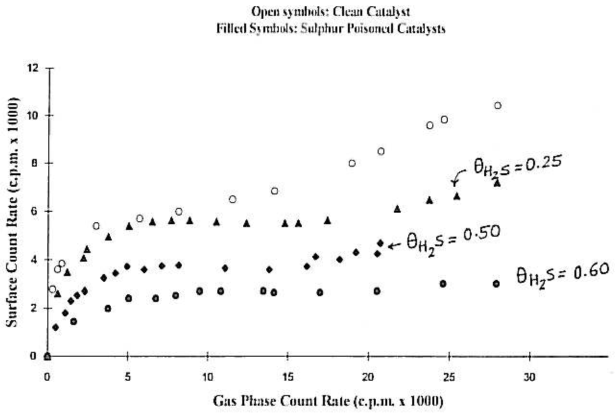


Fig. 7. Adsorption of ^{14}C-carbon monoxide on clean- and sulphur-poisoned Europt-1 at 293±2K.

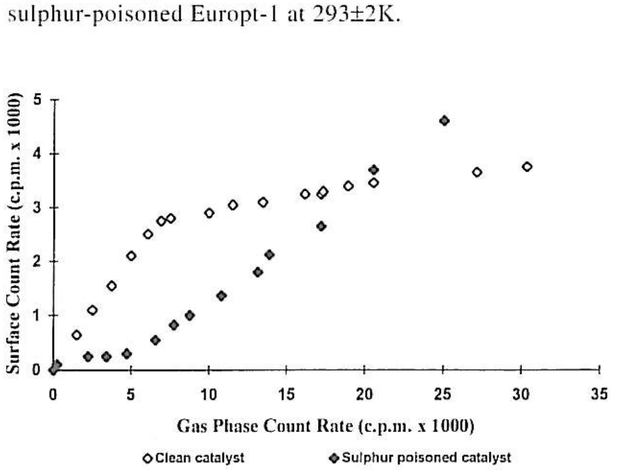


Fig. 8. Adsorption of ^{14}C-carbon monoxide on clean- and sulphur-poisoned Europt-3 at 293±2K.

On (Europt-3), and at $H_2S = 0.25$, the sulphur poisoned catalyst showed an isotherm indicating an initial small ^{14}CO uptake with a short plateau region followed by a linear increase of ^{14}CO adsorption, as further gas pressure was admitted on the catalyst. The latter behavior was also observed in ethene adsorption isotherm and attributed to physical adsorption process.

Effects of ^{35}S-H_2S Poisoning on the Selectivity of ethyne Hydrogenation

In a series of ethyne hydrogenation reactions using different Pt-catalysts, the selectivities on these catalysts was studied as a function of H_2S-uptake. Controlled pulses of ^{35}S-H_2S were admitted to the catalyst surface and left to equilibrate for 15 minutes, followed by 15 minutes evacuation of the reaction vessel. A 6.66 Kpa, 3:1, H_2:C_2H_2 mixture was then introduced on to the catalyst in the reaction vessel and the extent of the reaction was monitored by the pressure transducer. At pressure fall of 1.33 Kpa, the products were analysed by the gas chromatography. This procedure was repeated with various amounts of pre-adsorbed H_2S.

Figure 9, shows the variation of selectivity with H_2S-coverage (H_2S). From these results it can be seen that, over (Europt–1) (6% Pt/SiO_2) and (0.8% Pt/SiO_2) catalysts, the selectivity decreased considerably as the pressure of H_2S was increased. The effect was greater with the former catalyst as compared with the latter. On (Europt-3) (0.3% Pt/Al_2O_3) and (0.8% Pt/Al_2O_3) catalysts, the presence of sulphur was beneficial in that a steady increase in the selectivity occurred as the H_2S-coverage was increased. This may be attributed to the influence of the acidic sites present on the alumina. This is indeed a possible explanation when the adsorption isotherms of ethyne and ethene on the sulphur-poisoned catalysts are compared with those obtained on the clean catalysts (Figs. 4, 6). The shapes of the secondary adsorption regions of these isotherms continued to increase sharply as further hydrocarbon gas was admitted to the catalyst. This latter behavior, which has been observed in the adsorption of n-pentane on various supports, such as carbon and $BaSO_4$, is characteristic of a physical adsorption process[13,15]. Thus, the possibility exists that, in the presence of sulphur, the gas phase ethene formed from ethyne hydrogenation being adsorbed at the chlorinated alumina sites, while the double bond character of the molecule was retained[16]. This, in the presence of hydrogen, would lead to the desorption of ethene to the gas phase, hence, increasing the selectivity.

When ^{35}S-H_2S was pre-mixed with the reaction mixture (3:1, H_2:C_2H_2) before the hydrogenation reactions on clean catalysts, the effect of sulphur on the selectivity with each catalyst was identical to that observed above. It is important to note that the presence of sulphur did not completely poison the catalysts for ethyne hydrogenation, and hydrogen effectively competes with sulphur for the sites suggestd above as active for both hydrogen dissociation and sulphur adsorption in the presence of ethyne and ethene. However, there is a strong evidence in the literature[17] to suggest that sulphur has a minor effect on the reactivity of the sites which were active for hydrogen adsorption.

The hydrogenation of ethyne in the presence of ^{14}C-ethene as a tracer was also examined on sulphur-poisoned catalysts, to gain further knowledge of the effect of sulphur on the different reaction pathways in ethyne hydrogenation on (Europt-1) which has been studied previously[4]. Samples of (Europt-1) were reduced and poisoned with known amounts of ^{35}S-H_2S and then a pre-mixed mixture of 1.66 Kpa C_2H_2, 5.0 Kpa H_2 and 0.27 Kpa $14C_2H_4$ was admitted to the reaction vessel. In another set of reactions the amount of added $^{14}C_2H4$ was increased to 0.5 Kpa and 0.67 Kpa. The content of radioactivity in the individual reaction products was determined using radio-gas chromatography. As observed on the sulphur-free catalysts, the amount of ^{14}C-ethane (C_2H_6) produced constituted only a small fraction (~ 1%) of the total ethane yield, relative to the amount expected from the amounts of added ^{14}C-C_2H_4 present in the reaction vessel.

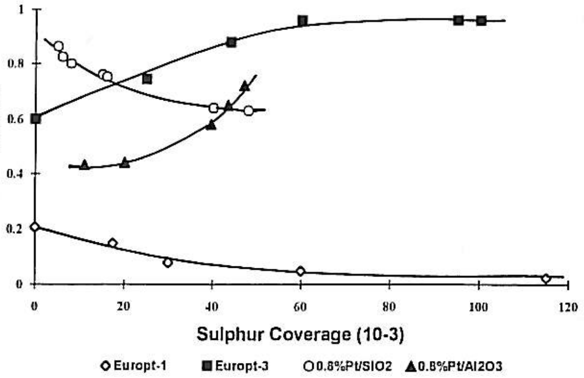
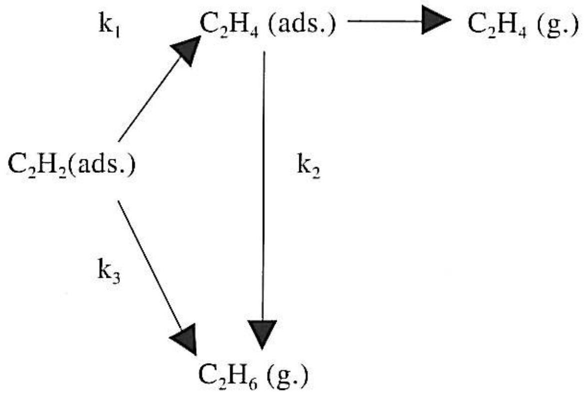


Fig. 9. Variation of selectivity with H_2S coverage (θH_2S) for ethyne hydrogenation on Pt-supported catalysts for ethyne hydrogenation at 293±2K.

The proposed pathways for ethyne hydrogenation on the supported-Pt catalysts used in this work[4,5,9] are:



It is possible to calculate relative values for the rate constants k_1, k_2 and k_3, using a developed steady state procedure[18] and values of k_1 = 0.020 3.5%; k_2 = 0.006 0.13% and k_3 = 0.066 0.08% were obtained for ethyne hydrogenation on sulphur-poisoned (Europt-1). When these rate constants are compared with the values of k1= 0.014 3%; k_2 = 0.002 4% and k_3 = 0.091 1%, obtained for ethyne hydrogenation on clean (Europt-1)[4], an interesting feature emerges. While the effect of sulphur was to decrease the hydrogenation rate occurring via the route k_3, it showed a beneficial effect in that an increase in the rate of the reactions proceeding via the routes k1and k_2 (k_1 k_2 k_3) leading to C_2H_6 formation. These findings suggest that the presence of one sulphur atom on a given site neither affected the catalytic activity or the selectivity of the neighboring sites (pure site effect) nor the mechanism of ethyne hydrogenation on these catalysts proposed previously[4,5]. For this reason (Europt-1) displayed a substantial decrease in the selectivity as the catalyst was poisoned with sulphur (Fig. 9). Similar behavior has been also observed in the hydrogenation of buta–1,3-diene on sulphur poisoned (Europt-1) and (Europt-3) catalysts[20].

CONCLUSIONS

In conclusion, the results obtained in this study of sulphur poisoning on Pt/SiO_2 and Pt/Al_2O_3 catalysts at 293 2K showed:

(i) During sulphur adsorption and at H_2S 0.5, a rearrangement of the surface occurs resulting in the freeing of metal sites on the surface. The precise origins of this rearrangement cannot be established from the present studies, however, it could arise from the movement of metal atoms through the sulphur species adsorbed in the primary layer.

(ii) The poisoning effects of sulphur are simply due to hydrocarbon site-blocking effect and not to ligand or electronic effects usually observed in sulphur poisoning[17].

(iii) The ^{35}S-H_2S tracer studies of sulphur poisoning presented in this work support our previous proposal[4,5,20] that the turning point observed in the hydrocarbon adsorption isotherms corresponds to a surface reconstruction process and ethyne hydrogenation takes place in the ad-layer (the secondary adsorption region) on the hydrocarbonaceous layer.

(iv) Sulphur promotes the adsorption of ethene and carbon monoxide on the acidic sites of the support material such as, Al_2O_3.

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REFERENCES

[1] Oudar, J. 1980. Sulphur adsorption and poisoning of metallic catalysts. *Catal. Rev. Sci. Eng.*, **22**, 171–195

[2] Bartholomew, C. H., Agrawal, P. K. and Katzer, J. R., 1982. Sulphur poisoning of metals. *Adv. Catal.*, **31**, 136–235.

[3] Barbier, J., 1985. Effect of poisons on the activity and selectivity of metallic catalysts. In J. Oudar and H. Wise (eds.). *Deactivation and Poisoning of Catalysts*, **3**, 109–150. Marcel Dekker Inc.

[4] Arafa, E. A. and Webb, G., 1993. A ^{14}C-Radiotracer study of the hydrogenation of ethyne over EUROPT-1. *Catal. Today*, **17**, 411–418.

[5] Arafa, E. A., 1998. A ^{14}C-Radiotracer study of the hydrogenation of ethyne on 0.3% Pt/Al2O3 (Europt-3). *Petroleum Res. J.*, **10**, 31–37.

[6] Bond, G.C. and Wells, P.B., 1985. Characterization of the standard platinum/silica catalyst Europt-1. *Appl. Catal.*, **18**, 225–230.

[7] Musso, J. C. and Parera, J. M., 1987. Adsorption and spillover of hydrogen on Al_2O_3 and Pt/Al2O3. *Appl. Catal.*, **30**, 81–90.

[8] Arafa, E. A., 1988. *Ph.D. thesis*, Glasgow University.

[9] Al-Ammar, A. S. and Webb, G., 1978. Hydrogenation of acetylene over supported metal catalysts. *J. Chem. Soc., Faraday Trans. I*, **74**, 195–205; 657–664.

[10] Bonzel, H. P. and Ku, R., 1973. Kinetics of sulphur adsorption on supported catalysts. *J. Chem. Phys.*, **58**, 4617; **59**, 1641.

[11] Protopopopoff, E. and Marcus, P., 1986. Coadsorption of sulphur and hydrogen on platinum. *Surface Sci.*, **169**, 237–244.

[12] Barbouth, N. and Salame, M.,1987. Influence of adsorbed sulphur on catalytical activity of platinum in ethylene hydrogenation reaction. *J. Catal.*, **104**, 240–245.

[13] Arafa, E. A., 1985. *M. Sc. thesis*, Glasgow University.

[14] Somorjai, G. A., 1990. Modern concepts in surface science and heterogeneous catalysis. *J. Phys. Chem.*, **94**, 1013–1023.

[15] Satterfield, C. N., 1980. *Hetrogenous Catalysis in Practice*. McGraw-Hill. 320 P.

[16] Peri, J. B., 1964. *Proceedings 3rd International Congress in Catalysis*. **2**, 1100.

[17] Oudar, J., 1986. Sulphur poisoning of metal catalyst. *Proceedings International Symposium in Heterogeneous Catalysis*. 245–250, ACS, New York.

[18] Berndt, G. F., Thomson, S. J. and Webb, G., 1983. Radiotracer studies of the hydrogenation of acethylene over nickel catalysts. *J. Chem. Soc. Faraday Trans.*, **79**, 195–207.

[19] Bond, G. C. and Burch, R., 1983. Metal-Support Interactions. In: G. C. Bond and G. Webb (eds.), *"Catalysis", Specialist Periodical Reports*, **6**, 27–60. The Chemical Society, London.

[20] Arafa, E. A., 1998. ^{35}S-Radiotracer studies of sulphur poisoning of platinum supported catalysts: 1. Hydrogenation of Buta–1,3-diene, *Proceedings 4th Arab Conference on Peaceful Uses of Atomic Energy*, Tunisia.