Petroleum Res. J. Vol. 10 (1998); P. 31-38, 7 Figs.

A ^{14}C-Radiotracer Study of the Hydrogenation of Ethyne on 0.3% $Pt/A1_2O_3$ (Europt-3)

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التقفّى بالأثر الأشعاعي للكربون -14 في دراسة هدرجنة الإيثاين على سطح المحفز $Pt/A1_2O_3$

عز الدين أحمد عرفة

تمت دراسة إمتزاز أول أكسيد الكربون والمواد الهيدروكربونية الإيثان والإيثين بنظام مغلق عند درجة حرارة 293±2K باستخدام طريقة التقفى بالأثر الأشعاعي لعنصر ^{14}C، إمتزاز أول أكسيد الكربون بيّن السلوك المتوقع (التشبع عند ضغوط محددة) بينما إمتزاز الإيثان والإيثين تم بمرحلتين أولية وثانوية. وجد أو حوالي 30% من المواد الهيدروكربونية تبقى مُمتزة على سطح المحفز ولا يمكن سحبها بالخلخلة أو بتشبيع المحفز بالهيدروجين ولا بإجراء تفاعلات هدرجنة للإيثين.

تمت هدرجنة الإيثاين على سطح المحفز على مرحلتين، خلال المرحلة الأولى حسبت درجة التفاعل وكانت 1.73±0.06 بالنسبة للهيدروجين و 0.95±0.01- بالنسبة للإيثاين وثابت معدل التفاعل كان $2.4\pm0.1 \times 10^{-2}$ لكل دقيقة وبطاقة تنشيط تساوي 40.7±0.01كيلو جول لكل مول كما أن إنتقائية المحفز لتكوين الإيثين كانت 0.68.

أوضحت مراقبة سطح المحفز خلال عملية الإمتزاز أو تفاعلات هدرجنة الإيثاين أو الإيثين لا يمتز بالمواقع الحساسة لإمتزاز الإيثاين بينما الأخير يمتز بمواقع إمتزاز الأول. كما تبين أنه خلال تفاعل الهدرجنة يتم غمر سطح المحفز بالمواد الهيدركربونية خلال المراحل الأولى للتفاعل وأن المسلك الرئيسي لتكوين الإيثان (C_2H_6) يتم بالهدرجنة المباشرة للإيثاين.

تم تمييز عدد ثلاثة مواقع لهدرجنة (i) الإيثاين إلى الإيثين، (ii) الإيثاين إلى الإيثان (iii) والإيثين إلى الإيثان. أقترح أن سطح المحفز يمر بمرحلة إعادة بناء حيث يتم تكوين مواقع لإمتزاز الإيثاين والإيثين تحت ظروف إمتزاز المواد الهيدروكربونية وهدرجنتها.

Abstract: *Abstract Using the ^{14}C-radiotracer technique the adsorptions of carbon monoxide, ethene and ethyne have been studied in a static system at 293±2 K. ^{14}CO adsorption showed the Langmuir-type behaviour whilst the adsorption of both ^{14}C-ethene and ^{14}C-ethyne showed typical primary and secondary adsorption regions. A fraction ca.30% of the adsorbed hydrocarbon retained on the surface as strongly bound species and cannot be removed by evacuation, dihydrogen or ethyne hydrogenation treatments.*

Ethyne hydrogenation on Europt-3 proceeds in two distinct stages. During the first stage the reaction order is ca. 1.73±0.06 in dihydrogen and is ca. - 0.95±0.01 for ethyne. The reaction rate constant is ca. $2.4\pm0.1 \times 10^{-2}$ min-1 with an activation energy of ca. 40.7±0.3 k Jmol^{-1}. The initial selectivity for ethene formation is ca. 0.68.

Direct surface monitoring during the adsorption or hydrogenation reaction shows that ethene does not adsorb on the ethyne adsorption site whilst ethyne adsorb on ethene adsorption site. Evidence has been obtained to show that during the hydrogenation reaction, surface coverage by hydrocarbon progressively increases at the

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commencement of the reaction and decreased linearly as the reaction proceeded.

The hydrogenation of ethyne in the presence of ^{14}C-ethene show that the yield of ethane from the hydrogenation of ethene constitute a very small fraction; the major route to ethane formation is by direct hydrogenation of ethyne. Three distinct types of surface sites are proposed as being responsible for the hydrogenation (i) ethyne to ethene; (ii) ethyne to ethane and (iii) ethene to ethane.

It is proposed that under the influence of hydrocarbon adsorption and hydrogenation reaction, the surface undergoes some reconstruction in which distinctive sites for the adsorption of ethyne and ethene are created.

INTRODUCTION

The hydrogenation of ethyne has been the subject of extensive investigations. It was first studied by Sheridan *et al.*[1,2] over pumice-supported metals, by Bond *et al.*[3,4] using alumina-supported metals and metal powders and more recently by Webb and his co-workers[5-9] on a range of supported Group VIII metal catalysts. The different aspects of the reaction have been reviewed by many workers[10-12].

Most of the early studies[1-4] were concentrated in evaluating the reaction kinetics and thermodynamic parameters to deduce the reaction mechanisms. The latter studies in particular, those employing the tracer technique[5-9], were carried out with the intention to sense the behaviour of the reactants during the adsorption and catalysis processes on clean and working catalysts in order to verify the deduced mechanisms.

It is generally accepted that the selectivity for ethene formation is associated with a thermodynamic factor which controls the relative surface coverage of ethyne and ethene (the same surface site being assumed to be involved in the adsorption of ethyne and ethene, i.e. depends on ΔH_{ads}.) and a mechanistic factor, which determines the extent to which the ethene is hydrogenated to ethane without undergoing intermediate desorption step (i.e. it is the catalyst property). The basis and extent to which the two factors operate either separately or together is not thoroughly clear, however, the reported studies indicate dependence on a number of variables in the system, such as, the activation energies of adsorbed and desorbed species[1-3], hydrocarbon: dihydrogen ratio[4], catalyst preparation and pretreatments[5-9] and type of support[12].

This paper is an extension to our previously reported studies[8] on ethyne hydrogenation over supported Group VIII metal catalysts and reports the adsorption of carbon monoxide, ethene and ethyne hydrogenation over the standard reference EUROPT-3, (Pt/Al_2O_3) catalyst[13].

EXPERIMENTAL

Catalyst

The catalyst used in this study is a standard catalyst containing 0.3% (w/w) Pt/Al_2O_3-0.82%Cl designated by the Council of Europe Catalysis Group as EUROPT-3 and has the industrial code KETJEN-CK303. The catalyst has a BET surface area of 184 m^2g^{-1} and pore volume of 0.49 cm_3g^{-1} [13].

Materials

^{14}C-carbon monoxide was prepared by the reduction of ^{14}C-carbon dioxide using metallic zinc as described elsewhere[5]. ^{14}C-ethene and ^{14}C-ethyne were supplied by the Radiochemical Centre, Amersham, of specific activities 5.8 mCi $mmol^{-1}$ and 1.08 mCi $mmol^{-1}$ respectively. Before use, each ^{14}C-labelled gas was diluted with the respective non-radioactive gas (B.O.C. Ltd) to give specific count rates of ca. 400,000 counts min^{-1} Po^{-}.

Apparatus

The adsorption and hydrogenation measurements were made in a reaction vessel of a similar design to that described earlier[5]. The reaction vessel (416 cm^3) was fitted with two inter-calibrated Geiger-Muller (GM) counters (Mullard MX168/01) to permit direct observation of the adsorbed species, during subsequent treatments and hydrogenation of hydrocarbons. The apparatus was maintained at a pressure of 0.0133 Pa by means of mercury diffusion pump backed by a rotary oil pump. Pressures in the reaction vessel were measured using a calibrated pressure transducer (S.E.Type SE/V/10D) capable of

accurately recording pressure change as low as 1.33 Pa.

To faciliate analysis of the gas phase on contact with the catalyst surface during the adsorption or subsequent surface processes, the reaction vessel was connected to a gas-sampling system which was coupled to a combined gas chromatograph-proportional counter. Analysis was performed using a 1.0 m (2.0 mm, i.d.) stainless-steel column packed with 40-60 mesh activated silica (Aerosil, Degussa Ltd). The column was operated at 313 K with helium (Air Products Ltd) as the carrier gas at a flow rate of 60 cm^3 min^{-1}. On elution from the column, the eluant was mixed with the required amount of methane (Air Products Ltd) before it entered the gas proportional counter.

Procedure

For catalyst reduction, the catalyst (typically 0.30±0.05g) in a finely divided form (100 B.S.S. mesh) was spread uniformly in a glass boat-shaped container and positioned in a part of the reaction vessel which was surrounded by an electric furnace. Dihydrogen was introduced to the catalyst at a flow rate of 30 cm^3min^{-1}, the temperature of the catalyst was raised at 5 $Kmin^{-1}$ to 523 K and maintained at this temperature for 2 h. The reaction vessel was then evacuated at 523 K for 30 min and the catalyst cooled *in vacuo* to ambient temperature.

A sample of Europt-3 was calcined in air at 773 K for 28 h, reduced in flowing dihydrogen at 673 K for 4 h and was then evacuated at 673 K for 30 min before being cooled to ambient temperature.

Adsorption of ^{14}C-carbon monoxide and ^{14}C-hydrocarbons was investigated by admitting small aliquots of the relavent gas to the reaction vessel, determining surface and gas-phase count rates after ~10 min equilibration (each determination is an average of triplicate measurements).

In the hydrogenation of ethyne a premixed 1:3 ethyne/dihydrogen mixture ratio at a total pressure of 6.67 kPa was admitted to the reaction vessel. The reaction was followed by the pressure fall recorded by the pressure transducer, samples being extracted at any desired pressure fall (% conversion) for analysis. All the adsorption and hydrogenation measurements were made at 293±2 K.

RESULTS AND DISCUSSION

Adsorption of ^{14}C-Carbon Monoxide

The adsorption isotherms obtained by admitting successive aliquots of ^{14}C-carbon monoxide to freshly reduced, deactivated (steady state catalyst) and calcined catalysts are shown in Figure 1. The adsorption on a freshly reduced catalyst showed the expected behaviour, the surface count rate increased linearly with increasing gas pressure until a plateau region was obtained, characteristic of Langmuir-type adsorption isotherm. The plateau region however, showed a slight positive gradient, such behaviour has been observed on a silica supported platinum catalyst (EUROPT-1)[8] and on oxidised copper surfaces[14]. The extent of ^{14}CO adsorption on a steady state catalyst is reduced remarkably to ca. 30% of that obtained on freshly reduced catalysts. This behaviour has also been encountered on supported Ni, Pd, Ir and Rd catalysts[5,7] and interpreted as due to adsorption of carbon monoxide in a linear mode on single metal sites left vacant following the dissociative adsorption of ethyne.

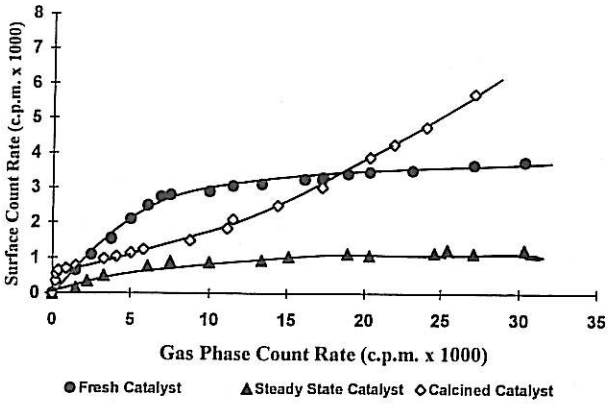


Fig. 1. Adsorption of ^{14}C-carbon monoxide on europt-3 at 293±2 K.

The adsorption of ^{14}CO on a freshly reduced calcined sample of the catalyst showed no plateau region as the gas pressure was increased. This behaviour suggests that treatment of Europt-3 in oxygen at 673 K tend to lower its dispersion and severely oxidize platinium atoms.

The effects of various treatments on the adsorbed carbon monoxide were also investigated, and the results are summarised in Figure 2. From these it can be seen that ca. 23% of the adsorbed ^{14}CO can be removed by evacuation and a further ca. 30% fraction can only be removed by cycles of dihydrogen - evacuation - ethyne hydrogenation treatments, however, ca. 47% of the adsorbed ^{14}CO is retained by the catalyst as strongly bound species. Kramer *et al.*[15] from their CO temperature programed desorption studies on Pt/SiO^2 catalyst identified such tightly bound CO species to be CO adsorbed at the phase boundary platinum/support in a slow adsorption process which may correspond to the primary adsorbed species of the adsorption isotherm (Fig.1) and in agreement with our findings such species can only be removed by cycles of oxidation-reduction at ~750 K.

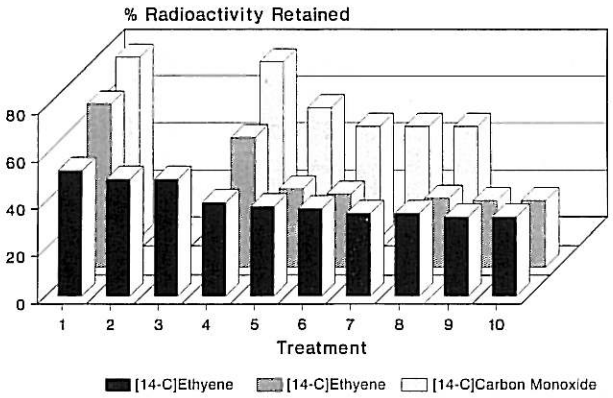


Fig. 2. Variations in surface count rates when a precovered surface was subjected to various treatments at 293±2 K.: 1.evacuation (30 min); 2.ethyne hydrogenation; 3.evacuation (30 min); 4.dihydrogen (13.33 k.pa for 15 h); 5.ethyne hydrogenation; 6.ethyne hydrogenation; 7.dihydrogen (13.33 k. pa. for 15 h); 8.ethyne hydrogenation; 9.dihydrogen (13.33 k. pa. for 15 h); 10.ethyne hydrogenation.

Adsorption of ^{14}C-Ethene and ^{14}C-Ethyne

The adsorption isotherms of ^{14}C-ethyne and ^{14}C-ethene on freshly reduced samples of Europt-3 catalysts are shown in Figures 3 and 4 respectively. They are of a similar form to the isotherms observed previously on Pt/SiO^2 (Europt-1) catalyst[8] and over the other supported Group VIII metals[5-7], showing a non-linear primary region and a linear secondary region. The extent of adsorption in the secondary region continued to increase with increasing adsorbate pressure, no plateau was reached even though gas pressures >0.7 Kp were used. When samples of the catalyst were precovered with C_2H_x species or run to their steady-state by sucssessive hydrogenations using 1:3 ethyne:dihydrogen mixtures and followed by ^{14}C-hydrocarbon adsorption, only the secondary adsorption region is observed (Figs. 3 and 4). Comparision of the amounts of ^{14}C-ethyne adsorbed on the primary region of a freshly reduced catalyst with the corresponding value for the adsorption of ^{14}C-carbon monoxide shows that the ratio of ethyne to carbon monoxide molecules on the surface is ca. 0.7:1.0 while the ratio of ethene to carbon monoxide is ca.0.2:1.0. The same ratios were also found to hold on steady-state catalysts. Assuming as generally accepted that ethyne and ethene adsorption occur as dissociative species, these results suggest that ~30% of the surface, for geometric reasons, not available for ethyne adsorption and ~80% of the surface sites for the same reason are unable to accomodate ethene molecules. These findings with the observations that no adsorption of ethene was observed to occur on ethyne precovered surfaces, whilst on ethene precovered surfaces, subsequent adsorption of ethyne resulted in a displacement of ca.50% of the pre-adsorbed ethene, clearly indicate that ethene adsorption occur on distinctive sites wherease ethyne adsorption can take place on more than site type. No ethene was ever observed as a self-hydrogenation product from the adsorption of ethyne.

The gas-phase hydrocarbon in contact with the surface during the build-up of the ^{14}C-ethyne and ^{14}C-ethene adsorption isotherm was analysed by radio-gas chromatography. This showed that during the build-up of the primary region (up to the turning point in the adsorption isotherm) the only hydrocarbon in contact with the surface was ethane.

The effect of subsequent treatments on ^{14}C-ethyne or ^{14}C-ethene precovered surfaces is shown in Figure 2. Note that about 70% of the adsorbed ^{14}C-hydrocarbons were effectively be removed by cycles of evacuation-ethyne hydrogenation-dihydrogen treatments at ambient temperature and the remaining ~30% of the ^{14}C-hydrocarbon species retained strongly adsorbed on the surface and can completely be removed by reduction in flowing dihydrogen cycles at 523 K.

Ethyne Hydrogenation Reactions

For the hydrogenation of ethyne at 1.67 kPa with dihydrogen at 5.0 kPa over 2.0±0.5g catalysts, plots of pressure against time curves showed that the reaction to occur in two distinct stages, the onset of the second stage being accompanied by an increase in rate at a pressure fall of ca. 1.67±0.027 kPa and ascribed to ethene hydrogenation in availability of dihydrogen[6]. Up to this acceleration point, the reaction order is ca. 1.73±0.06 in dihydrogen and ca. - 0.95±0.01 for ethyne with a rate constant of ca. 2.4 0.1 x 10^{-2} min^{-1} and an activation energy of ca.40.7± 0.3 kJ mol^{1}.

When series of ethyne hydrogenation reactions were performed over the same catalyst sample, it was observed that from reaction to reaction the activity progressively decreased until a steady-state activity was attained. Both the first and second stages of ethyne hydrogenation were deactivated by similar amounts. Treatment of a freshly reduced catalyst with ethyne alone for extended periods, before carrying out the hydrogenation reactions, did not have any significant effect on the deactivation process. From this and similar observations on Group VIII metal catalysts[5-9], it can be suggested that the deactivation does not simply arise from a build-up of carbidic or other hydrogen defficient carbonaceous residues on the surface, resulting from the dissociative adsorption of ethyne, but rather from a process involving the interaction of ethyne with dihydrogen on the catalyst surface. Such a thought has been previously coined by Thomson and Webb[12] in which they proposed that the hydrogenation on metals should be interperated as hydrogen transfer between an adsorbed hydrogen-defficient hydrocarbon species, M-CxHy, and adsorbed alkene and alkyne, rather than the direct addition of hydrogen to an associatively adsorbed hydrocarbon. The deactivation process did not have any effect upon the acceleration point of the reaction, although the selectivity, S, which defined as: $S = P_{ethene} / (P_{ethene} + P_{ethane})$ increased by ca. 6% as the catalyst run to its steady-state activity. The average selectivity for ethene formation over Europt-3 is ca. 0.677±1.8%.

Regeneration of Europt-3 can be achieved by heating at 573 K in flowing pure dihydrogen (30 cm^3 min^{-1}) for 2 h and evacuation at 573 K for 30 min (Figs 3 and 4).

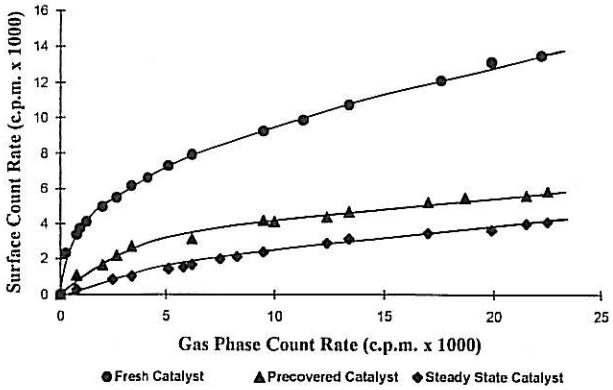


Fig. 3. Adsorption of ^{14}C-ethyne on europt-3 at 293±2 K.

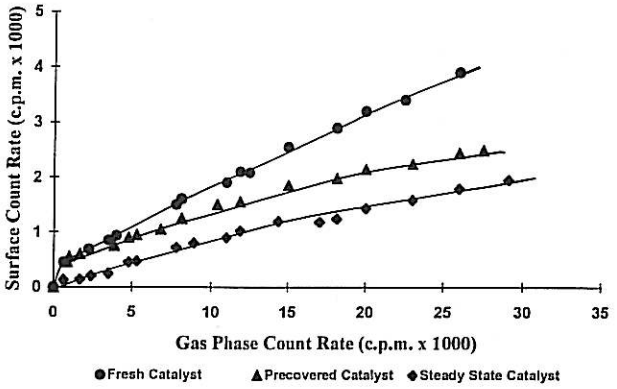


Fig. 4. Adsorption of ^{14}C-ethyne on europt-3 at 293±2 K.

Ethyne hydrogenation on clean and steady-state samples of Europt-3 was followed by monitoring the surface radioactivity during the course of the reaction. The results presented in Figure 5, showed that when a 1:3 ^{14}C-ethyne:dihydrogen mixture reacted on clean or steady-state catalysts, the surface radioactivity representing the adsorbed ^{14}C-species increased almost sharply at the comencement of the reaction and then decreased linearly as the reaction proceeded, this extent is more pronounced on clean catalyst in comparision on deactivated catalyst. This implying the formation of surface monolayer coverage on the freshly reduced surface and the adsorption of ^{14}C-species on the metal sites made available following ethyne hydrogenation on the steady-state catalyst.

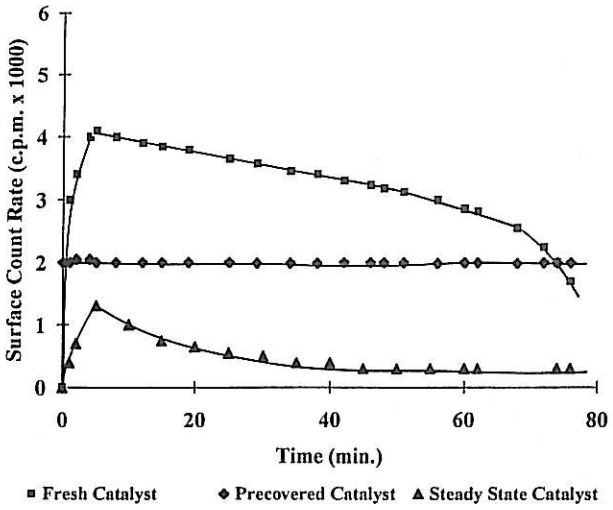


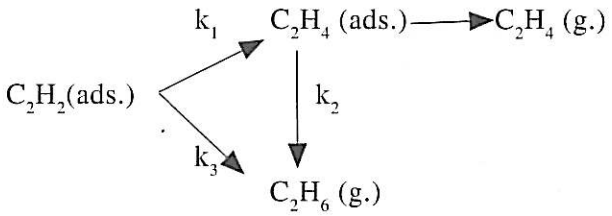
Fig. 5. Variations in surface count rate during the hydrogenation of 1.67 k. pa. ^{14}C-ethyne with 4.99 k. pa. dihydrogen on europt-3 at 293±2 K.

When the catalyst was precovered with pressures of ^{14}C-ethyne capable of building up the primary region of the adsorption isotherm and followed by 1:3 ^{12}C-ethyne:dihydrogen mixture reaction on the same catalyst, the surface radioactivity remained unchanged during the course of the reaction (Fig. 5). This is another evidence to support the suggestion made earlier from the ^{14}C-hydrocarbon adsorption behaviour that, catalysis of ethyne hydrogenation takes place on the secondary adsorption region.

Hydrogenation of 12C-Ethyne + ^{14}C-Ethene Mixtures

In order to gain some insight into the mechanism of the selective hydrogenation of ethyne over Europt-3, a series of reactions were carried out on steady-state catalysts using 1:3, ethyne:dihydrogen and varied aliquots of ^{14}C-ethene which were added to the reaction mixture before admission to the reaction vessel. The amount of radioactivity in the individual reaction products was determined by radio-gas chromatography. The results are shown in Table 1. From these, two interesting features emerge, first, the amount of ^{14}C-ethane constitutes a small proportion of the total ethane yield relative to the amount expected from the amounts of added ^{14}C-ethene and the ^{12}C-ethene present in the reaction vesel. This suggests that only minute amounts of ethene undergo readsorption and further hydrogenated to ethane until all of the ethyne has hydrogenated. Secondly, the yield of ^{14}C-ethane increased linearly as the reaction proceeded and was directly proportional to the amount of ^{14}C-ethene added to the reaction mixture.

Using the data of Table 1 and the possible routes for the hydrogenation of ethyne presented below:



the relative values of the rate constants were calculated according to the procedure of Brendt *et al.*[7] and found to equal: k_1= 0.071±4% , k_2= 0.009±3.3% and k_3= 0.163±4% at 293±2 K.

CONCLUSIONS

The obtained results of the adsorption of carbon monoxide, ethyne and ethene and the hydrogenation of ethyne on Europt-3 are of similar characteristics to those shown by Europt-1 and other supported Group VIII metals[5-9]. The adsorptions of ^{14}C-hydrocarbons occur in two distinct stages; a non-linear primary region followed by a linear secondary region and ethyne hydrogenation is associated with hydrocarbon species adsorbed on the secondary region.

The results of the ^{14}C-hydrocarbon adsorptions together with the ^{14}C-ethene tracer studies show the presence of separate surface sites for the hydrogenation of ethyne to ethene, the hydrogenation of ethyne to ethane and the hydrogenation of ethene to ethane. This consistent with a mechanism previously proposed by Webb and co-workers[7,8] for the hydrogenation of ethyne over supported Group VIII metal catalysts as shown in Figure 6.

Although the precise population of these different surface site types is difficult to assess, however, from the extent of ^{14}C-carbon monoxide and hydrocarbons adsorptions and using the rate constants presented above they can roughly be estimated to represent, Type I sites = 29.2%,

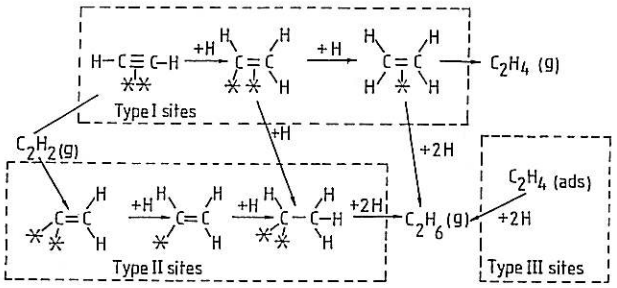


Fig. 6. Surface site types responsible for ethyne hydrogenation on supported metal catalysts.

Type II sites = 67.1% and Type III sites = 3.7%. Collectively, the results of this study concludes that Europt-3 catalyst shows a high thermodynamic selectivity but a low mechanistic selectivity.

From the ^{14}C-adsorption studies and ethyne hydrogenation reactions over Europt-3 and on the other supported Group VIII metal catalysts studied[5-9], we conclude that during the adsorption of hydrocarbons or ethyne hydrogenation, a rearrangement of the surface occurs resulting in the freeing of metal sites on the surface. The precise origins of such rearrangement cannot fully be established from the present studies. It could, however, arise due to the movement of some metal atoms through the hydrocarbonaceous primary layer, under the influence of the hydrogenation reaction or adsorbed hydrocarbons as predicted in Figure 7. Such phenomenon has been observed in the hydogenation of hydrocarbons on supported Ni and Pt catalysts and termed corrosive chemisorption[16,17].

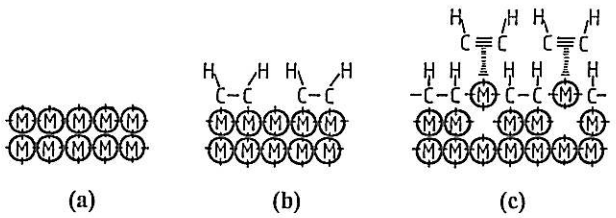


Fig. 7. Model for surface reconstruction as a result of adsorption or catalysis of hydrocarbons on supported catalysts. (a) clean surface; (b) hydrocarbon covered surface; (c) reconstructed surface.

According to such surface rearrangement model, the deactivation of the Group VIII metal catalysts to a steady-state activity could be interpreted as the establishing of a steady-state concentration of active metal sites by migration of individual metal atoms into the hydrocarbanaceous layer adsorbed on the primary region, these metal atoms being responsible for the secondary adsorption process and catalysis. The presence of the carbonaceous overlayer causes a modification of the surface orbitals to the extent that distinct sites for the adsorption of ethyne and ethene, as -bonded complexes are created.

Table 1. Variation of product composition (in pascal) as a function of extent of hydrogen uptake during the hydrogenation of 12C-ethyne in the presence of varied amounts of added 14C-ethene at 293(2 K

Conversion (%)	$P(^{12}C_2H_4)$	$P(^{12}C_2H_6)$ *(Total)*	$P(^{12}C_2H_6)$ *(Direct)*	$P(^{14}C_2H_6)$
		^{14}C-ethene = 133.3 Pa		
20.0	184	43	39	2.7
41.9	335	109	101	2.9
75.9	536	165	151	3.3
91.2	661	252	228	4.8
		^{14}C-ethene = 266.6 Pa		
13.1	128	21	17	7.2
45.0	372	48	36	8.3
93.0	528	212	188	10.9
113.7	575	247	221	11.9
		^{14}C-ethene = 666.6 Pa		
10.9	97	21	19	13.2
40.1	235	129	123	17.3
65.4	413	179	167	17.6
105.6	543	279	257	24.4

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