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Hydrogenation of Acetylene over Supported Metal Catalysts

Part 4.—[14C]Tracer Studies of the Reaction Catalysed by Nickel-Silica

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The hydrogenation of acetylene, at low pressure, has been studied over a 25.4% w/w nickel-on-silica catalyst at 293 K. Under the conditions used, the acetylene was hydrogenated to ethylene and ethane, with the selectivity for ethylene formation being 76%. Some n-butane was also formed during the later stages of the reaction.

Adsorption of [¹⁴C]acetylene on the catalyst, in the absence of hydrogen, showed two regions in the adsorption 'isotherm'. The species adsorbed in the primary region, identified from [¹⁴C]carbon monoxide adsorption studies as being hydrocarbon adsorbed directly on the metal, was not directly involved in the catalysis. The extent of this adsorption diminished as the catalyst was brought to its steady-state activity, when the rate of reaction was approximately one-sixth its initial value, by successive hydrogenation reactions. Hydrogenation of [¹⁴C]acetylene showed that during the course of the reaction, the acetylene surface coverage passed through a maximum, which was attained at the point corresponding to the acceleration point in the pressure-fall-time curve for the reaction.

Hydrogenation of $[^{12}C]$ acetylene + $[^{14}C]$ ethylene mixtures showed that the predominant reaction pathway to ethane formation was a direct route from acetylene, rather than *via* ethylene as an intermediate

$$C_2H_2 \xrightarrow{k_1} C_2H_4$$

values of $k_1 = 0.089$, $k_2 = 0.0042$ and $k_3 = 0.0163$ being evaluated.

The results are interpreted in terms of four types of sites on the catalyst surface which are responsible for acetylene self-hydrogenation, conversion of acetylene to ethylene, ethane production from acetylene and the hydrogenation of ethylene to ethane. These sites also account for the selectivity of the catalyst in acetylene hydrogenation.

In Parts 1-3 of this series¹⁻³ we reported studies of the adsorption and hydrogenation of acetylene and ethylene, and of the effects of added ethylene and carbon monoxide upon the hydrogenation of acetylene on supported palladium, rhodium and iridium catalysts. These showed that the adsorption of [¹⁴C]acetylene and [¹⁴C]ethylene occurred in two distinct stages; a primary region, located on the metal, comprised of hydrocarbonaceous species resulting from dissociative adsorption of the hydrocarbon and a secondary region consisting of associatively adsorbed hydrocarbon, probably located in an ad-layer on top of the primary adsorbed species. Hydrogenation catalysis was associated with the hydrocarbon species adsorbed on the secondary region. Evidence was also presented to show that on working catalysts under acetylene-hydrogenation conditions, the adsorption and subsequent hydrogenation of acetylene and ethylene occurred at independent surface sites, although, as shown by [¹⁴C]ethylene tracer experiments, the subsequent hydrogenation of ethylene was not of major importance for the production of ethane during acetylene hydrogenation.

HYDROGENATION OF ACETYLENE

The major factors controlling the selectivity in the acetylene hydrogenation were the abilities of the metals to promote separate reaction pathways to the direct formation of ethylene and ethane from adsorbed acetylene.

Guczi *et al.*,⁴ using a double labelling technique involving ¹⁴C and deuterium, also drew similar conclusions. On palladium black catalysts, direct conversion of acetylene to ethane, by a route not involving the formation of ethylene as an intermediate, was of major importance in determining the selectivity.

We have extended our studies to include nickel-silica catalysts to examine, in more detail, the build-up of carbonaceous surface deposits during acetylene adsorption and hydrogenation and the relevance of such species to catalytic hydrogenation, and to examine the general applicability of the model for selective hydrogenation proposed in our earlier studies.

EXPERIMENTAL

The catalyst contained 25.4% w/w nickel supported on Aerosil-200 silica (Degussa). It was prepared by the homogeneous precipitation of nickel hydroxide onto the silica by addition of urea to an aqueous solution of nickel nitrate in which the silica was suspended and which was maintained at 363 K. After precipitation the supported hydroxide was freed of ammonium nitrate by several washings with distilled water. The supported material was spray dried and stored until required.

The supported hydroxide was reduced and activated *in situ* in a stream of hydrogen (*ca.* $25 \text{ cm}^3 \text{ min}^{-1}$) at 723 K and 1 atm* for 18 h, followed by evacuation at 673 K for 6 h before cooling *in vacuo* to ambient temperature. Temperature-programmed reduction studies showed that a small amount of the nickel remained unreduced, probably as nickel silicate. However, as the higher temperatures required to effect complete reduction resulted in extensive sintering of the metal, the lower-temperature reduction was used throughout and this led to reproducible activity from sample to sample. The apparatus was similar to that described previously¹⁻³ and enabled pressure changes during hydrogenation to be measured, product distributions to be determined and the behaviour of ¹⁴C-labelled molecules to be observed both on the surface of the catalyst, in the gas phase and in the products.

RESULTS

All adsorption and hydrogenation measurements were made at 293 ± 2 K using hydrocarbon pressures in the range 0-12.5 Torr.[†]

ACETYLENE HYDROGENATION AND CATALYST DEACTIVATION

For the reaction of 12.5 Torr acetylene with 37.5 Torr hydrogen over 0.082 g Ni/SiO_2 , the pressure-time curves (fig. 1) showed that the reaction proceeded in two distinct stages, the onset of the second stage being accompanied by an increase in rate. The first stage of the reaction was found to be first order in total pressure, except for the first 1-3 min, as shown in fig. 2.

Analysis of the reaction products during the course of the reaction showed that in the initial stages, where deviation from first-order behaviour was observed, ethane was the sole product. Thereafter both ethane and ethylene were produced, the selectivity (S), defined as S = R - ((R - 1)R)

$$S = P_{C_2H_4} / (P_{C_2H_4} + P_{C_2H_6})$$

having a constant value of 0.76 ± 0.01 during the second phase of the reaction up to the acceleration point in the pressure-time curves. After the acceleration point the major process was the further hydrogenation of ethylene to ethane, although in the

- * 1 atm \equiv 101325 Pa.
- † 1 Torr \equiv (101325/760) Pa.

196

latter stages of the reaction some n-butane, constituting up to 15% of the final products, was produced.

Fig. 3 shows that the rate of hydrogenation, as determined from the linear portion of the first-order plots, decreased with successive reactions until a constant 'steady-state' activity was attained. The reaction rate did not tend to zero.



FIG. 1.—Pressure fall against time curves observed for the reaction of 12.5 Torr acetylene with 37.5 Torr hydrogen over freshly reduced nickel-silica catalyst (0.082 g) at 293 K. ●, Reaction (1); ①, reaction (5); ○, reaction (10).



FIG. 2.-First-order plots from pressure fall against time curves shown in fig. 1.

Simultaneously, the rate of the second stage of the reaction, after the acceleration point, also decreased to a steady value.

When yields of ethane and ethylene and the pressure fall for acetylene are plotted against time, the graphs show a small acceleration, fig. 4(A) and (B). Catalyst deactivation could only be achieved by using acetylene + hydrogen reaction mixtures. When the catalyst was treated with 12.5 Torr acetylene alone over a prolonged period of several hours, no deactivation was observed. Deactivation had no effect upon the catalyst selectivity.

The original activity of a deactivated catalyst could be reproducibly restored by reduction in a flow (30 cm³ min⁻¹) of hydrogen at 1 atm and 773 K for 4 h, followed

HYDROGENATION OF ACETYLENE



FIG. 3.- Variation of first-order rate constant with number of reactions performed over 0.082 g freshly reduced nickel-silica catalyst; $(P_{C_2H_2})_0 = 12.5$ Torr; $(P_{H_2})_0 = 37.5$ Torr.



FIG. 4.—Variation of pressures of acetylene (●), ethylene (●) and ethane (○) during reaction of 12.5 Torr acetylene with 37.5 Torr hydrogen over 0.082 g nickel-silica catalyst. (A) Freshly reduced catalyst; (B) steady-state catalyst.

by evacuation at 723 K for 2 h and cooling *in vacuo* for a further 2 h. During this regeneration methane was produced as the major product, together with small amounts of ethane.

ADSORPTION OF [14C]ACETYLENE

On a freshly reduced catalyst sample (0.49 g), the adsorption isotherm for $[^{14}C]$ acetylene was of the form shown in fig. 5. The isotherm is of similar shape to those observed previously using supported rhodium, iridium and palladium catalysts,^{1, 2} consisting of a steep 'primary' region and a linear 'secondary' region.

Analysis of the gas-phase material in contact with the surface during the build-up of the primary region showed that this consisted solely of [¹⁴C]ethane. Once the primary region was complete the gas phase consisted of the ethane formed initially, together with acetylene; ethylene was not observed to be formed at any stage during the acetylene adsorption.

The possible participation of the acetylenic species adsorbed on the primary region in the hydrogenation catalysis was examined. The surface was covered with $[^{14}C]$ acetylene to the point corresponding to completion of the primary region. A $[^{12}C]$ acetylene (12.5 Torr) + hydrogen (37.5 Torr) reaction mixture was admitted to the precovered surface. Monitoring of the surface during the subsequent hydrogenation



FIG. 5.—Adsorption of $[^{14}C]$ acetylene (11.80 μ Ci mmol⁻¹) on a freshly reduced nickel-silica catalyst (0.049 g).



FIG. 6.—Adsorption of [¹⁴C]acetylene (11.80 μ Ci mmol⁻¹) at various stages of deactivation of a 0.049 g sample of nickel-silica to a steady-state activity (S).

and analysis of the reaction products by radio–gas chromatography showed that no $[^{14}C]$ acetylene was removed from the surface during the hydrogenation. A small amount of the preadsorbed $[^{14}C]$ acetylene could be removed by allowing the catalyst to stand under the hydrogen-rich reaction products for 1 h following the reaction.

The adsorption of [14C]acetylene was investigated at various stages during the deactivation of the catalyst to its steady state. After each acetylene hydrogenation reaction the catalyst was allowed to stand under the reaction product mixture for 1-16 h before evacuation, followed by determination of the isotherm. Fig. 6 shows the [14C]acetylene isotherms at various points on the deactivation curve. In each case the surface count rates were corrected for background activity arising from permanently retained acetylenic residues, which progressively increased as the deactivation process proceeded until, in the catalyst steady state, the primary region was effectively covered with these residues. The deactivation process had no effect upon the linear secondary region.

SURFACE RADIOACTIVITY DURING HYDROGENATION OF $[^{14}C]$ acetylene

It had been expected from conventional Langmuir-type models of acetylene hydrogenation that admission of [14C]acetylene and hydrogen (12.5 and 37.5 Torr, respectively) to a freshly reduced catalyst (0.153 g) would have led to an instant build-up to full coverage of a surface layer of [14C]acetylene which would diminish during reaction. When this was investigated the very reverse was found to be true, as is shown in fig. 7. When such catalysts, after the initial [14C]acetylene reaction, were subjected to further batch hydrogenations using [12C]acetylene only *ca.* 2% of the surface radioactivity was removed per run.



FIG. 7.—Variation of the surface (\bigcirc) and gas-phase (\bigcirc) count rates with time and the corresponding pressure fall against time curve observed during the hydrogenation of 12.5 Torr [14C]acetylene (11.80 μ Ci mmol⁻¹) with 37.5 Torr hydrogen over a freshly reduced nickel–silica catalyst (0.049 g).



FIG. 8.—Adsorption of [14C]carbon monoxide $(27.0 \ \mu \text{Ci} \, \text{mmol}^{-1})$ on a freshly reduced (\bigcirc) and steady-state (\bigcirc) nickel-silica catalyst (0.049 g), and on freshly reduced catalyst after evacuation (dotted line) and treatment with an acetylene + hydrogen reaction mixture (\bigcirc).

ADSORPTION OF [¹⁴C]CARBON MUNOXIDE

Fig. 8 shows the adsorption isotherm for $[^{14}C]$ carbon monoxide on a freshly reduced sample (0.049 g) of Ni/SiO₂. Evacuation of the covered surface resulted in a decrease in the surface count rate from a saturation value of 2060 to 1515 c.p.m. (fig. 8).

After evacuation, treatment of the catalyst with acetylene + hydrogen mixtures did not result in any further displacement. However, admission of a further quantity of [¹⁴C]carbon monoxide to the treated catalyst resulted in an increase in the saturation surface count rate to 2255 c.p.m.; this represented an increase of *ca*. 10% in the carbon monoxide adsorption capacity of the surface following the acetylene hydrogenation. Similar behaviour has been observed with rhodium catalysts used for allene hydrogenation.⁵

Adsorption of [14C]carbon monoxide on a steady-state catalyst resulted in a very low saturation surface count rate corresponding to only 3.9% of the adsorption capacity of the freshly reduced catalyst, as shown in fig. 8.



FIG. 9.—Variation of the pressures of acetylene (\diamond), ethylene (\bigcirc) and ethane (\square) with conversion for the hydrogenation of 12.5 Torr acetylene with 37.5 Torr hydrogen over a steady-state nickel-silica catalyst (0.0816 g) in the presence of 3 Torr (open symbols), 2 Torr (filled symbols) and 1 Torr (half-filled symbols) added [14C]ethylene. [Conversion (%) = 100 × moles H₂ consumed per mole acetylene present.]

$[^{14}C]$ ethane production in acetylene hydrogenation in the presence of $[^{14}C]$ ethylene

The addition of small amounts of [¹⁴C]ethylene to acetylene + hydrogen reaction mixtures provides a method whereby information may be obtained about possible reaction pathways in the acetylene hydrogenation.

Fig. 9 shows the results obtained when 1.0, 2.0 and 3.0 Torr of $[^{14}C]$ ethylene were added to the acetylene (12.5 Torr) + hydrogen (37.5 Torr) reaction mixture before its admission to 0.0861 g steady-state catalyst. The results show how limited is the incorporation of $[^{14}C]$ ethylene into the product ethane. In these tracer experiments the production of ethylene and ethane and the fall in acetylene pressure are shown in fig. 10. The selectivity, taking into account the added ethylene, appeared to be unchanged.

DISCUSSION

This discussion will deal with various features of the hydrogenation of acetylene over silica-supported nickel: the mechanism of the reaction, the deactivation of the catalyst, the adsorption of acetylene and ethylene and of carbon monoxide on fresh



FIG. 10.—Variation of ethylene (\Box) and ethane (\bigcirc) counts, recorded in chromatograph eluant, during the hydrogenation of 12.5 Torr acetylene with 37.5 Torr hydrogen over a steady-state nickel-silica catalyst (0.082 g) in the presence of 3 Torr (open symbols), 2 Torr (half-filled symbols) and 1 Torr (filled symbols) added [¹⁴C]ethylene (13.1 μ Ci mmol⁻¹). (1 Torr = 4940 counts.)

and on deactivated catalysts, the possible role of hydrogen and comparisons with supported rhodium, iridium and palladium catalysts. We begin, however, with a brief statement of current beliefs about acetylene hydrogenation. Bond and Wells⁶ have reviewed the field, where thermodynamic and mechanistic arguments have been considered in accounting for the selectivity of the reaction in which ethylene, and not ethane, is the predominant product. Recently, McGown *et al.*⁷ have produced evidence for involvement of different types of sites for acetylene and ethylene hydrogenation. This idea of a mechanistic explanation for selectivity was proposed by Bond *et al.*⁸ in 1958. In contrast, a single-site model was that finally chosen by Guczi *et al.*⁴ to explain the deuteration of acetylene in the presence of [¹⁴C]ethylene on palladium black. They proposed the existence of a single type of site on which acetylene was converted in parallel reactions to ethylene and ethane; later in the reaction this site converted ethylene to ethane.

Thus in our analysis of the results obtained over supported nickel it seems that we have to resolve two problems: whether or not there are multiple sites involved and if there is a single or multiple pathway in the hydrogenation of acetylene to ethane.

In the hydrogenation of [¹⁴C]acetylene on a fresh catalyst the familiar Langmuir-type model for strongly adsorbed acetylene would have produced an acetylene monolayer at the start of the reaction.

McGown *et al.* calculate that for a palladium–alumina catalyst acetylene is 2000 times more strongly adsorbed than ethylene, both being more strongly adsorbed than hydrogen.

The actual adsorption is quite different, as shown in fig. 7. It is negligible at the start and rises to a maximum over 10 min when most of the acetylene has been hydrogenated.

The second feature we observed in acetylene hydrogenations was an acceleration process, fig. 4. The curvatures observed for loss of acetylene and generation of ethylene cannot be reproduced by any first- or second-order process. Acceleration was most likely to have occurred by the generation of active sites. The rise in surface count rates typified in fig. 7 suggests that these active sites might be carbonaceous species. Though carbon loss, to the surface, or acetylene polymerisation might account for some of this curvature for acetylene, the growth of gas-phase ethylene indicates acceleration.

Considering the problem of whether the formation of ethane arises from further hydrogenation of ethane (step k_2 in the reaction scheme) or by direct hydrogenation of adsorbed acetylene (step k_3 in the reaction scheme),

$$C_2H_2 \xrightarrow{k_1} C_2H_4 \\ \downarrow k_2 \\ \downarrow k_3 \\ C_2H_6$$

if reaction progress is measured not in time but in terms of hydrogen uptake (H), where 200% represents complete conversion, linear plots arise where the k represent rates with respect to hydrogen uptake. Then using equations of the type $dB/dH = k_1 - k_2$, the amounts present at any stage of the reaction can be expressed as

$$A = A_0 - (k_1 + k_2) H$$
$$B = B_0 + (k_1 - k_2) H$$
$$C = C_0 + (k_2 + k_3) H$$

where A, B and C are the amounts of C_2H_2 , C_2H_4 and C_2H_6 , respectively. The amount of radioactive ethylene present at any stage of the reaction, B^* , is governed by its dilution from acetylene hydrogenation and losses to ethane. Thus

$$B^* = B_0^* - k_2 [B^*/(B^* + B)] H$$

from which it can be shown that

$$B^* = B_0^* [B_0 + k_1 H - k_2 H) / (B_0 + k_1 H)].$$

Using the experimental data from fig. 11 where 3 Torr [¹⁴C]ethylene was added at the start of the reaction we can calculate $k_1 + k_3 = 0.106$, $k_1 - k_2 = 0.085$ and $k_2 + k_3 = 0.02$. Using the further information that at H = 100, $B^* = 11975$ counts and $B_0^* = 12417$ counts, we find values as follows:

$$k_1 = 0.089, \quad k_2 = 0.0042, \quad k_3 = 0.0163.$$

These values can now be tested on the experimental run with 1 and 2 Torr added $[^{14}C]$ ethylene. Fig. 11 shows excellent agreement between predicted and calculated values.

If we now examine the situation where k_3 is considered to be zero, the observed values of pressures allow us to calculate $k_1 = 0.106$ and $k_2 = 0.02$. If these values are used to predict the [1⁴C]ethylene radioactivity B^* , which is given by $B^* = B_0^* - k_2(B^*/B) H$, the results shown by the dotted lines in fig. 11 are obtained. Clearly there is a discrepancy between the observed and calculated behaviour and we conclude that our results indicate that the predominant route to ethane formation is by direct hydrogenation of adsorbed acetylene (step k_3).

When successive acetylene hydrogenations were performed on the same catalyst sample, the rate decreased from reaction to reaction until a steady-state activity was attained. The changes occurring on the catalyst during this deactivation were, therefore, probed by examining the adsorption of [¹⁴C]acetylene on the surface.

Comparison of the adsorption isotherms for [14 C]carbon monoxide (fig. 8) and [14 C]acetylene (fig. 5) on freshly reduced nickel catalysts shows that whereas the former reaches a saturation value, consistent with the formation of a monolayer of the adsorbate, the hydrocarbon isotherms exhibit both a 'primary' and a 'secondary' region, being of a similar form to those observed with supported noble-metal catalysts.¹⁻³ Comparison of the surface count rates at saturation for carbon monoxide

203

HYDROGENATION OF ACETYLENE

and at the turning point from primary to secondary regions in the acetylene isotherm shows that after correction for differences in specific activity, the ratio [CO(ads.)/ $C_2H_2(ads.)$] = 0.64. Primet *et al.*⁹ have suggested that for the adsorption of carbon monoxide on nickel-silica catalysts at room temperature, the average bond number is 1.85, with linear, bridged and multicentre carbon monoxide species being formed. Assuming, as seems reasonable, that the carbon monoxide saturation values correspond to monolayer coverage of the metal, we may conclude that the maximum value for the average bond number of the acetylene adsorbed on the primary region is 1.18. This value is surprisingly low and a value in excess of 2 might well be expected,¹⁰ but could arise if polymerisation of the primary adsorbed species occurs. The average composition of the primary acetylenic species on freshly reduced catalysts can be calculated from the amounts of ethane formed to be $C_2H_{1.9}$, implying at least some dissociation of the acetylene.



FIG. 11.—Variation of [14C]ethylene counts with conversion for the hydrogenation of 12.5 Torr acetylene with 37.5 Torr hydrogen in the presence of 1 Torr (\bigcirc), 2 Torr (\bigcirc) and 3 Torr (\bigcirc) added [14C]ethylene. Circles represent experimental points; solid lines are calculated variations according to the reaction scheme, assuming $k_3 \neq 0$; dotted lines are calculated variations assuming $k_3 = 0$. [The dashed line was used to calculate k values (see text).]

Selective labelling of the primary region with [¹⁴C]acetylene shows that the acetylenic species adsorbed on this region do not directly participate in the catalysis, in the sense that they do not appear as reaction products, although a fraction of them can be removed as ethane and methane by extended treatment in hydrogen at the reaction temperature; this fraction progressively decreases as the steady-state activity is attained.

When [¹⁴C]acetylene adsorption was studied on a deactivated catalyst a different picture emerged, fig. 6. The primary region was much diminished and [¹⁴C]carbon monoxide adsorption revealed a reduction in free metal surface to 4% of its original value.

The deactivation process, observed only with the acetylene + hydrogen mixtures, but not with acetylene alone, corresponds to a progressive build-up of permanently retained hydrocarbonaceous species on the primary region. Using infrared spectroscopy, Sheppard and Ward¹¹ have .hown that, in the presence of hydrogen, acetylene adsorption on various metals results in the formation of hydrocarbonaceous polymers, although no such species are formed in the absence of hydrogen. Together these observations suggest that the deactivation is due to the formation of polymeric species on the primary region. The observation that the deactivation of the nickel catalyst had no effect upon either the selectivity or the relative activity of the catalyst for acetylene and ethylene hydrogenation (both stages of the acetylene hydrogenation, before and after the acceleration point, were equally affected) implies that the deactivation arises from some factor which acts upon a common feature of both reactions.

In the hydrogenation of acetylene, both in the presence and absence of added [¹⁴C]ethylene, it is significant that in the initial 10-15% of the reaction, the pressure-time curves showed deviation from first-order behaviour and that during these initial stages, the selectivity for ethylene formation was very low. Subsequent studies¹² have shown that with catalysts from the same stock, similar behaviour is observed when acetylene is admitted to the reaction vessel followed by hydrogen, and that the amount of ethane formed in this way is independent of the initial hydrogen pressure. Thus, the effect cannot be attributed to the more rapid diffusion of hydrogen to the surface on admission of the premixed reactants, thereby creating a hydrogen-rich surface. Contrary to our observations, this would also be expected to give an enhanced [¹⁴C]ethane yield in the initial stages of the hydrogenation of acetylene + [¹⁴C]ethylene mixtures.

Note that when acetylene alone is either admitted to a freshly reduced catalyst or left in contact with a steady-state catalyst for periods of approximately 30 min, self-hydrogenation with the formation of ethane occurs. However, ethylene is never observed as an acetylene self-hydrogenation product. Our observations are consistent with a model in which, on initial contact of the reaction mixture with the catalyst surface, a small amount of acetylene self-hydrogenation occurs independently of the true hydrogenation reaction and that this reaction gives rise to the relatively high yield of ethane initially.

It is important to note that since this 'self-hydrogenation' of acetylene occurs in each reaction, both on partially deactivated and steady-state catalysts, the sites responsible for this process are regenerated, either during the course of the subsequent reaction or by evacuation at the completion of the reaction. The process cannot be simply envisaged as a disproportionation of acetylene leading to the formation of ethane and carbonaceous material on the metal surface.

From the radiotracer results with added [¹⁴C]ethylene we may conclude that at conversions below those corresponding to the acceleration point, the further hydrogenation of ethylene to ethane is relatively unimportant in determining the selectivity of the catalyst. From the results shown in fig. 11 and from the constants derived for the reaction scheme, the amounts of ethane formed by the further hydrogenation of ethylene are insignificant.

In agreement with our earlier findings for supported noble-metal catalysts¹⁻³ and those of Guczi *et al.*⁴ for palladium blacks, we conclude that the origins of the selectivity in the nickel-catalysed reaction lie in the ability of the metal or the metal/C/H system to catalyse the direct hydrogenation of acetylene to ethane.

The occurrence of at least four separate and distinct reaction pathways can be identified from the present studies. These are:

$$C_2H_2 \rightarrow C_2H_6$$
 (self-hydrogenation) (1)

$$C_2H_2 + H_2 \to C_2H_4 \tag{2}$$

$$C_2H_2 + 2H_2 \rightarrow C_2H_6 \tag{3}$$

$$C_2H_4 + H_2 \to C_2H_6. \tag{4}$$

Although not extensively examined in this study, we did establish that changes in

the pressure of hydrogen altered rates significantly and leads us to comment on the role of hydrogen.

When the experiments for fig. 6 were being conducted it was observed that as the amount of primary adsorption which was possible was reduced during deactivation, the activity of the catalyst also diminished. This suggests some participation of the primary adsorbed species in the catalysis. We suggest that the role of these primary hydrocarbonaceous species is to control the effective concentration of hydrogen for the hydrogenation reaction in both the acetylene to ethylene and ethylene to ethane steps. Such a conclusion is consistent with our earlier proposals regarding the mechanism of the hydrogenation of unsaturated hydrocarbons¹³ involving hydrogen transfer between dissociatively adsorbed species located on the primary region and associatively adsorbed hydrocarbon located on the secondary region. The deactivation process must involve a decrease in the concentration of the catalytically active hydrogen-transfer species, probably by their incorporation in the permanently retained polymer.

Furthermore, since the deactivation has no effect upon the effective surface concentration of the acetylene, namely the secondary region (see fig. 6), we conclude that the deactivation arises from a decrease in the effective concentration of hydrogen. This may be achieved by a reduction in the concentration of the hydrocarbonaceous hydrogen-transfer species, as suggested above, and our observations suggest that this is a common species for acetylene and ethylene hydrogenation.

The identity of the surface sites responsible for reaction¹ is less clear. However, some indications as to their identity may be obtained from a consideration of the carbon monoxide adsorption results. The surprising feature to emerge from these results is the observation that the adsorption capacity of the catalyst for carbon monoxide is increased by its usage for acetylene hydrogenation. This enhanced adsorption could be due to spillover of carbon monoxide, although this is unlikely on nickel-silica at room temperature¹⁴ and, in any case, would be expected to occur without the necessary precursor of acetylene hydrogenation. Alternatively, it could be due to the presence of hydrogen. Wedler *et al.*¹⁵ and Horgan and King¹⁶ have observed enhanced carbon monoxide adsorption on nickel films in the presence of hydrogen at 353 and 300 K, respectively. However, tritium tracer studies of supported metals¹⁷ have shown that after evacuation the amounts of hydrogen remaining on the metal surface are small and are unlikely to be of sufficient quantities to give rise to a 10% increase in adsorption of carbon monoxide.

A third possible explanation of the enhancement is that the acetylene + hydrogen mixtures, on contact with the catalyst surface, give rise to a surface reconstruction and the creation of fresh adsorption sites. It is notable that in each reaction some n-butane is produced at a late stage in the acetylene hydrogenation. [¹⁴C]tracers also show that this is produced from an acetylene precursor, rather than from ethylene. We tentatively suggest that this process gives rise to isolated metal sites which are not available on the freshly reduced catalysts and which, therefore, give rise to enhanced carbon monoxide adsorption. Remembering that acetylene adsorption on clean metal gives rise to ethane production, as observed in our adsorption measurements, it is possible that these isolated sites may also be responsible for the rapid conversion of acetylene to ethane at the commencement of the hydrogenation reaction.

In conclusion, the results described above for the nickel-catalysed reaction are in general agreement with our earlier findings for supported noble-metal catalysts¹⁻³ and indicate that the model proposed for the selective hydrogenation of acetylene involving separate sites for the conversion of acetylene to ethylene and ethane, and for ethylene to ethane, is of general applicability. Further studies to attempt to identify

the precise nature of these sites and to determine the availability of hydrogen in the presence of the different hydrocarbons are currently being undertaken.

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(PAPER 2/884)