

Adsorption and Reactions of Ethyne

Effects of Modifiers and Formation of Bimetallics

**Nicolaas R. M. Sassen, Adrianus J. den Hartog, Fred Jongerius,
Jacques F. M. Aarts and Vladimir Ponec***

*Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden,
The Netherlands*

Adsorption of C_2H_2 and C_2H_4 has been studied with Pd(111) and Pd-Cu(111) single-crystal planes using EELS. The formation of dissociatively adsorbed species is controlled by ensemble size effects. The catalytic experiments performed with powder catalysts reveal that formation of bimetallics from an active and an inactive metal or diminishing the particle size increase the selectivity to ethene. This supports the idea that the increase is due to suppression of dissociatively adsorbed, possibly multiply bound, species.

Studies on selectivity of catalysts are becoming more frequent. Increasing prices of raw materials and energy on the one side and increasing environmental problems on the other force the industry to look for more selective catalysts. Knowledge concerning the selectivity in catalytic reactions is improving and its empirical character is slowly but steadily being converted into scientific theories.¹ However, we are still in the early stages of formulation of general principles governing selectivity.

An interesting field to explore is the selective hydrogenation of ethyne to ethene. A reaction which has been first treated as a system of purely consecutive reactions (C_2H_2 – C_2H_4 – C_2H_6) appeared to be a reaction with two parallel pathways to ethane:² one upon which intermediates do not leave the surface until they are fully hydrogenated and the other involving the already mentioned consecutive reaction. This paper attempts to identify the factors which influence the relative contributions of the two routes.

Experimental

Vibrational spectra have been obtained using an EELS apparatus (Leyboldt, Heraeus). A double-pass 127° monochromator and analyser allowed measurements with a resolution usually > 10 meV (80 cm^{-1}). All spectra were recorded in a specular mode.

Reactions of ethyne were studied in a static low-pressure apparatus (background pressure with powder catalysts *in situ* better than 10^{-6} Torr[†]); $C_2H_2/H_2 = 0.3$ and the total pressure was *ca.* 1 Torr. The products are analysed by means of a mass spectrometer through a continuous leak. The temperature range studied was 273–373 K. The products were analysed using the *m/e* peaks at 30, 27 and 26, respectively, for ethane, ethene and ethyne, whilst the whole fragmentation pattern was used to check the reliability of the analysis. The selectivity to ethene is defined as

$$S = \frac{[C=C]}{[C=C] + [C-C]} \times 100\%.$$

The bimetallic powders were prepared by coimpregnation (5 wt % loading) of SiO_2 with appropriate amounts of $Ir(NH_4)_2Cl_6$ and $CuCl_2$ or Au compounds dissolved in aqua regia and drying at 400 K followed by reduction. Particle sizes were determined

[†]1 Torr = 101 325/760 Pa.

by X-ray diffraction and were found to be *ca.* 7 nm for all catalysts. No extended alloy formation was found using this technique, by monitoring shifts in the peak position (and, of course, none are expected since these are systems with a limited solubility). Reduction at 670 K for 8 h *ex situ* was followed by reduction at 520 K for 8 h *in situ*.

A series of Ir catalysts with varying particle sizes was prepared as follows. The catalyst with 0.6% Ir loading and 1 nm (TEM) Ir particles was prepared by ion exchange of $\text{Ir}(\text{NH}_4)_2\text{Cl}_6$ with Na-zeolite (pH 12, NH_4OH) at 373 K. The catalyst with 0.7% Ir loading and 2 nm (TEM) particles was prepared by homogeneous precipitation,³ whereby $\text{Ir}(\text{NH}_4)_2\text{Cl}_6$ is precipitated as $\text{Ir}(\text{OH})_4$ by slowly decomposing (373 K) urea on the surface of silica. The catalyst with 2.5% Ir loading and particles of 5.3 nm (XRD line broadening) was prepared by a classical impregnation technique. The largest-particle Ir catalyst, 13 nm (XRD line broadening) was prepared by reducing a mechanical mixture of the precursor and SiO_2 with 10 wt % Ir.

All catalysts were calcined in oxygen (21 h) at 570–670 K, these temperatures being reached by slow heating ($0.5\text{--}1.0\text{ K min}^{-1}$). After flushing the catalyst with N_2 reduction took place, as with the bimetallics.

Results

The results presented below concern two topics: (a) chemisorption monitored by EELS when using single-crystal planes [Pd(111) and Pd/Cu(111)] as adsorbents, and (b) catalytic reaction followed in a closed static low-pressure apparatus, using Ir and Ir-bimetallics on SiO_2 powder catalysts. A certain (albeit loose) relation exists between (a) and (b) which justifies the simultaneous presentation. Discussion of the conclusions on the catalytic reaction is separated, but the discussion concerning the identification of species by EELS is included in this section.

EELS on C_2H_4 and C_2H_2 Adsorption

Adsorption of ethene, the product of ethyne hydrogenation or disproportionation, was monitored first. Fig. 1A shows the most typical result obtained with Pd(111). It should be mentioned that spectra of both ethene and ethyne show also a broad absorption at *ca.* 2900 cm^{-1} , and some spectra also exhibit a band due to traces of (background) CO. Our results on ethene adsorption (also those not shown here) are in good agreement with the literature.^{4,5} Bandy *et al.*⁵ collected convincing arguments that the 940 cm^{-1} band should be ascribed to π -complexed ethene. According to these authors π -complexed C_2H_4 is likely to be a precursor of other types of adsorption. On more reactive surfaces (*e.g.* Ni) the population of π -complexed C_2H_4 can be kept higher (at an observable level) by poisoning the surface; for example by deposition of a carbonaceous layer on it.

The pair of peaks at 1340 and 1090 cm^{-1} has been a matter of a longer discussion. Originally the peaks were ascribed to ethylidene ($=\text{CH}-\text{CH}_3$), but later stronger evidence was gathered for ethynyl ($\equiv\text{C}-\text{CH}_3$) being responsible for these peaks. The analysis by Skinner *et al.*⁶ of the i.r. data for the model compound $\text{CH}_3\text{C}\cdot\text{Co}_3(\text{CO})_9$ was decisive. These authors identified the vibrational frequencies of the CCH_3 group, which are in close correspondence with features observed in EELS for adsorbed C_2H_4 . Moreover, the intensity ratio of the symmetrical CH_3 deformation at 1340 cm^{-1} and the C—C stretch at 1090 cm^{-1} , which both belong to the same symmetry species, was found to be near unity in the i.r. and EEL spectra, implying a similar ratio for the relevant dynamic dipole moments. Fig. 1A also shows that when the system is heated the π -complexed C_2H_4 disappears and the ethynyl absorption grows.

Fig. 1 shows the most relevant part of the results obtained upon adsorption of ethyne. One can observe the following important features: (a) at the lowest exposures only

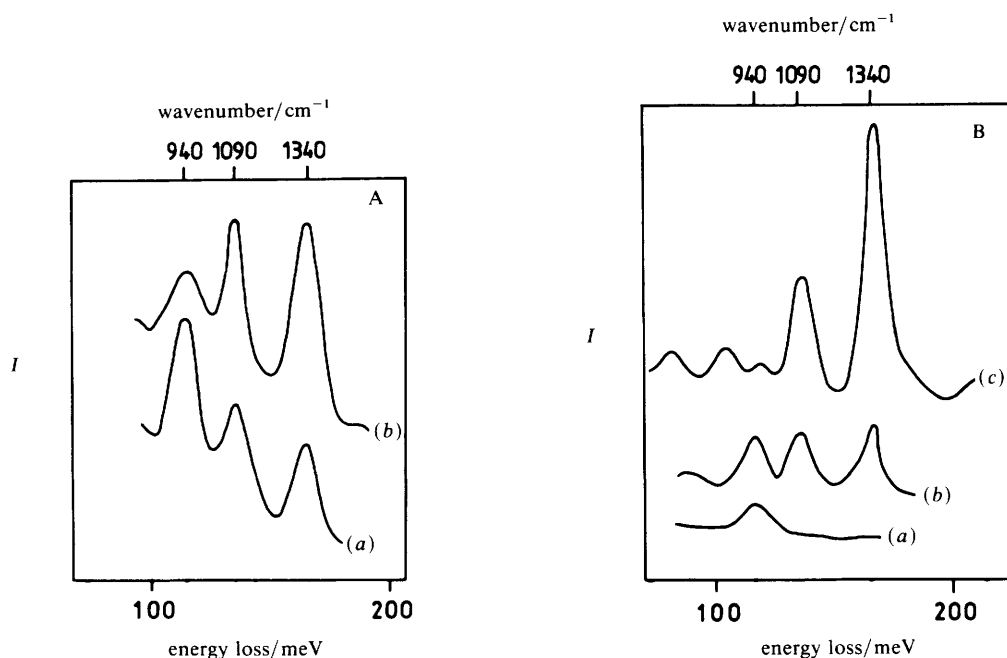


Fig. 1. (A) EEL spectra upon adsorption of C_2H_4 on Pd: (a) 3 L exposure at 253 K. Next to molecularly adsorbed (π -complex) C_2H_4 (940 cm^{-1}), ethylidyne is present (1340 and 1090 cm^{-1}); (b) spectrum after slow heating to 293 K. (B) Adsorption of C_2H_2 on Pd. Changes in spectra with increasing exposure: (a) 0.2 L, (b) 0.6 L, (c) 3 L.

π -complexed C_2H_4 is observed; (b) at higher exposures, formation of ethylidyne is observed, as characterized by the typical ethylidyne ratio $P=1.0$. At the highest exposures, when the surface becomes more crowded, the two peaks at 1340 and 1090 cm^{-1} no longer grow equally. P is now clearly greater than one. The most likely conclusion is that at least two species contribute to the pair of absorptions. Another interesting point is that the adsorption of the π -complexed C_2H_4 is diminished when ethyne is present at the highest exposure. The absorption at 940 cm^{-1} clearly decreases, since molecular ethene is displaced by ethyne.

It is not possible to ascribe at the moment the two other peaks (650 and 830 cm^{-1}) definitely. Let us mention only that molecular ethyne is expected to show bands in the 670 – 870 region,⁷ and benzene, formed by trimerization, shows two strong losses in the region 700 – 900 cm^{-1} .

Formation of C_2H_4 and C_2H_3 —* species upon adsorption of C_2H_2 shows that some molecules have gained an H atom. This can happen either by the known process of redistribution of hydrogen (disproportionation)⁹ or by traces of endogeneous hydrogen not removed upon evacuation and present even at pressures of the order of 10^{-10} Torr. Experiments with C_2D_2 showed that at least a part of the mentioned hydrogenated species is formed by endogeneous hydrogen (C_2H_4 was formed from C_2D_2).

Further adsorption of ethene and ethyne has been monitored on the (111) plane of a Pd/Cu alloy single crystal. According to an earlier study¹⁰ the sample with 75% Pd in bulk should have *ca.* 70% Pd in the outermost layer. When ethene is adsorbed on the Pd–Cu (111) surface, the molecular, π -complexed C_2H_4 can be observed again (930 cm^{-1}). When the surface is covered by ethene at 253 K to a high extent (exposure

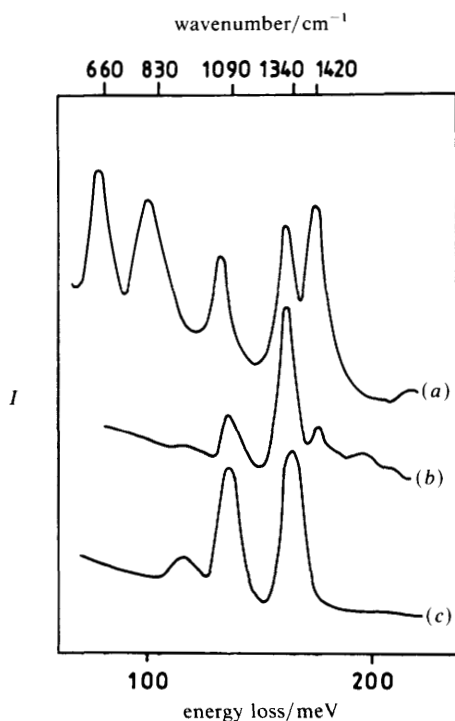


Fig. 2. EEL spectra upon adsorption of C_2H_2 on Pd/Cu (111): (a) surface saturated at 253 K (note the new loss at 1420 cm^{-1}); (b) after exposure of 6 L at 293 K the gas phase evacuated (the layer dehydrogenated by that) and C_2H_2 admitted again (4 L) (note the unequal growth of the two losses at 1090 and 1340 cm^{-1}); (c) exposure of 3 L at 293 K.

3 L)[†] and then slowly heated (1 K min^{-1}) molecular C_2H_4 was desorbed and no other species appeared. However, upon rapid heating (10 K min^{-1}) ethylidyne (1340 , 1090 cm^{-1} , $P=1$) appears. This shows that the formation of ethylidyne, a species multiply bound to the metal surface is less easy on Pd-Cu than on Pd, and upon slow heating C_2H_4 is desorbed more rapidly than it is converted into ethylidyne. Results obtained upon adsorption of ethyne on Pd-Cu are shown in fig. 2. Upon adsorption at 293 K (3 L), ethylidyne is mainly formed. When a carbonaceous layer is deposited first on the surface (6 L ethyne admitted and the gas phase evacuated for several hours) the exposure of additional ethyne (4 L) leads to a spectrum shown in fig. 2(b). We see that the ratio of intensities $I(1340)/I(1090)$ is considerably higher than unity, implying that another species is formed simultaneously with or instead of ethylidyne. We have seen that with pure Pd this situation could arise merely by admitting 3 L ethyne to the surface. With Pd-Cu [see fig. 2(c)] ethylidyne is the main product upon admission of 3 L ethyne, and a slightly more severe procedure is necessary to produce a surface (obviously a surface with a hydrogen-lean carbonaceous layer) on which the new species and/or ethylidyne are formed.

The observation of a strong peak at 1340 cm^{-1} and a weak one at 1090 cm^{-1} points to an adsorbate containing a CCH_3 group, but these peaks could also arise from a species which is different from ethylidyne. Although additional spectral evidence is lacking, we suggest that this species is ethylidene ($=\text{CH}-\text{CH}_3$) which is bound only

[†]1 L = 10^6 Torr s.

by a double bond (ethynidyne is triply bound) to a surface and which contains an additional H atom. A difference in the CC stretch and CH₃ deformation dynamic dipole moments would be then responsible for the change in the $I(1340)/I(1090)$ ratio. The tilt of the molecular axis can also have the following effect on the spectral visibility of vibration modes. The unperturbed symmetric deformation vibration of CH₃ would become less interacting and the perturbed asymmetric deformation vibration (a down-shift due to the interaction with the surface) would become more strongly interacting with the incoming field.

When ethyne is admitted to saturation level (*i.e.* no further change is observed upon a further increase in exposure) at 253 K, a complex spectrum is observed. Molecular ethyne is most likely responsible for the absorptions at 660 and 830 cm⁻¹; ethynidyne is present next to it and a new peak is observed at 1420 cm⁻¹. In compliance with the ideas expressed by other authors¹¹ we suggest that this is an absorption by a vinylidene group (C=CH₂). Next to it, bands which we saw also with pure Pd (only they are more intense here) at 660 and 830 cm⁻¹ are observed.

The industrial catalysts work under conditions at which the surface of the metal is most likely covered by a carbonaceous layer (a deposit with a very low H/C ratio). It is therefore interesting to see which changes occur in the spectrum after accelerated formation of such a layer. When a layer containing ethynidyne species is heated, ethynidyne decomposes and is possibly also desorbed. After heating to 473 K, the main absorptions which survive are at 750 and 2990 cm⁻¹ and they have been ascribed in the literature¹² to M—C_x—H_y vibrations ($x > y$). Such species have been observed with Pd, Pt, Ir and Ni, thus they are formed quite commonly. Their effect on ethyne adsorption is shown in fig. 3(b).

When heating of the adsorbed layer to 473 K is repeated, the species produced by dissociative adsorption suppress entirely the formation of ethynidyne upon re-admission of ethyne. Heating an adsorbed layer to 723 K produces a surface showing no detectable absorption which could be ascribed to any C—C or C—H vibrations. However, the influence of such a layer on a subsequent readsorption is the same as that exerted by the layer formed at 473 K. The surface with carbonaceous layers again shows absorptions which correspond with 'C=CH₂' like (vinyl and vinylidene group) vibrations. Obviously, these species appear upon ethyne adsorption only when the reactivity of the surface is first suppressed.

Working industrial catalysts are not only modified by other elements (Pb, S) or carbonaceous layers but also by exposure to the air (O₂). It is interesting to observe the consequences such exposure may have. Fig. 4 shows that after adsorption of oxygen at 293 K (3 L) on Pd—Cu(111), three peaks appear at 410, 830 and 1050 cm⁻¹. Such losses were also observed with Pd(111) and Ir(111) and also polycrystalline Cu.¹³ According to the literature a band at 850 cm⁻¹ has been ascribed to peroxo (O₂²⁻) species and a band at 1035 cm⁻¹ to superoxo (O₂⁻) species; the metal-atomic oxygen bond on Pd(111) absorbs at 500 cm⁻¹ and the metal-O₂ bond absorbs at 400 cm⁻¹. However, we believe that the bands observed here (with Pd—Cu) should be preferably associated with those bands which have been observed with Ir(111) after oxygen adsorption at 600–800 K. The latter paper ascribed the 800 cm⁻¹ loss to a surface oxide and the loss at 1005 cm⁻¹ has been related to the subsurface atomic oxygen.¹³ The temperature (293 K) is rather high to expect molecular forms of O₂ on Pd—Cu and, moreover, the observed bands remain in the presence of C₂H₂ and do not diminish at elevated temperatures. Oxygen vibrations disappear at *ca.* 800 K. Upon heating (293–800 K) the peak at 410 cm⁻¹ shifts to 390 cm⁻¹, that at 830 cm⁻¹ shifts to 700 cm⁻¹ and the highest-frequency loss shifts from 1000 to 1100 cm⁻¹.

When a surface precovered with oxygen (3 L exposure) is exposed to ethene only a small new peak appears at 1340 cm⁻¹. This indicates that the dissociative adsorption or shifts of hydrogen atoms leading to ethynidyne are substantially suppressed by oxygen

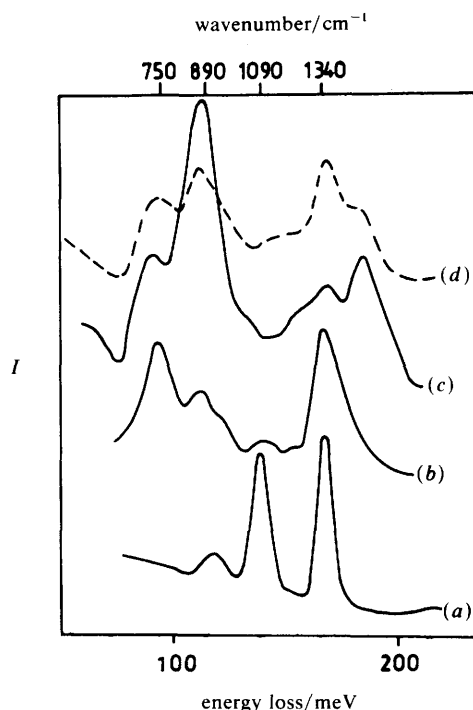


Fig. 3. EEL spectra upon adsorption of C_2H_2 on Pd/Cu(111): (a) after exposure of 3 L at 293 K; (b) the layer from (a) heated to 473 K, and admitting C_2H_2 after cooling down to 293 K (exposure 10 L); (c) obtained after exposure of 3 L at 253 K on a surface which was prepared in the following way to simulate the working surface of a catalyst: exposure of 3 L at 293 K, heating of a layer up to 723 K, sample cooled down in 10^{-7} Torr H_2 , sample evacuated; (d) the layer from (c) heated up to 293 K.

preadsorption (3 L). If a surface covered with oxygen (3 L exposure) is exposed to 10 L ethyne at 293 K the spectrum shown in fig. 4 is observed. We observe the oxygen losses again and next to them the dominating 1340 cm^{-1} loss with a shoulder at $1420\text{--}1450\text{ cm}^{-1}$. Loss at 740 cm^{-1} can most likely be attributed to a C_xH bond vibration. The spectrum also has a very intense C—H loss at 2990 cm^{-1} (not shown here). When this layer is annealed to 373 K, the 740 cm^{-1} loss gains intensity at the expense of the 1340 cm^{-1} loss. At 473 K the latter loss disappears completely. Above 473 K both C—H losses (740 and 2990 cm^{-1}) decrease and at 723 K the peak at 2990 cm^{-1} disappears completely. The peaks which remain (790 and 1090 cm^{-1}) are ascribed here to oxidic and sub-surface oxygen.

Summarizing, we see again that the presence of blocking species (oxygen atoms) suppresses the formation of ethylidyne and promotes the detectability of ethylidene and vinyl-group vibrations.

Catalytic Measurements

We have seen in the foregoing section that alloying of Pd with a less active metal, or the blocking of the surface (by O or C) suppresses the formation of the species bound to the metal surface by a bond with the highest multiplicity (3) and probably requires the largest ensemble of active (Pd) atoms. We expected that in parallel with this other

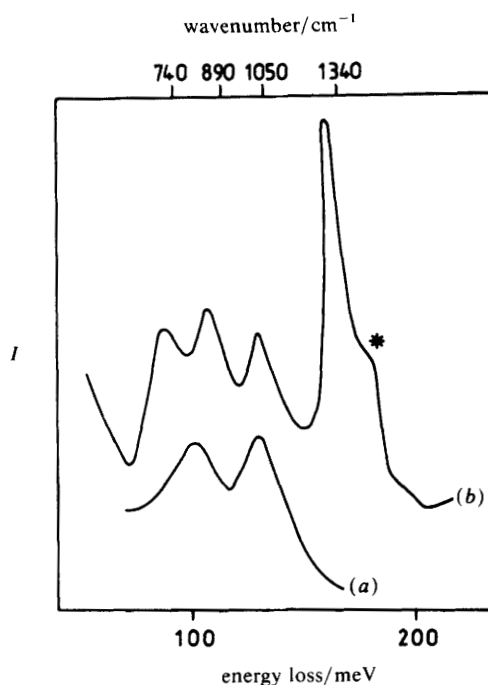


Fig. 4. EEL spectra upon adsorption of C_2H_2 on Pd/Cu(111) with preadsorbed oxygen: (a) preadsorbed oxygen, 293 K, 3 L. * = 1420–1450 cm^{-1} ; (b) adsorption of (10 L) C_2H_2 on the preadsorbed oxygen.

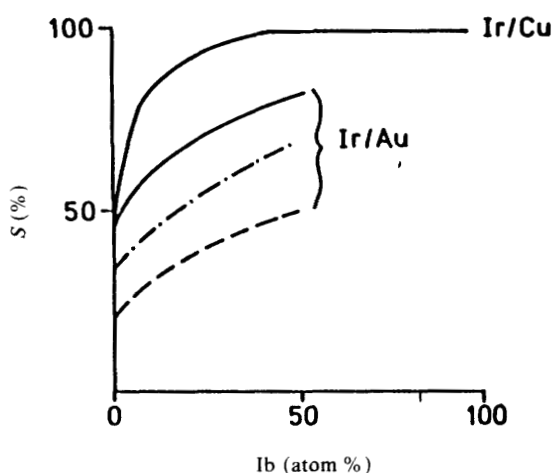


Fig. 5. Effect of Cu and Au on the selectivity to ethene of the Ir catalysts. Selectivity as a function of the content (atom %) of the Ib metal. (—) 373 K, (— · —) 323 K, (---) 295 K.

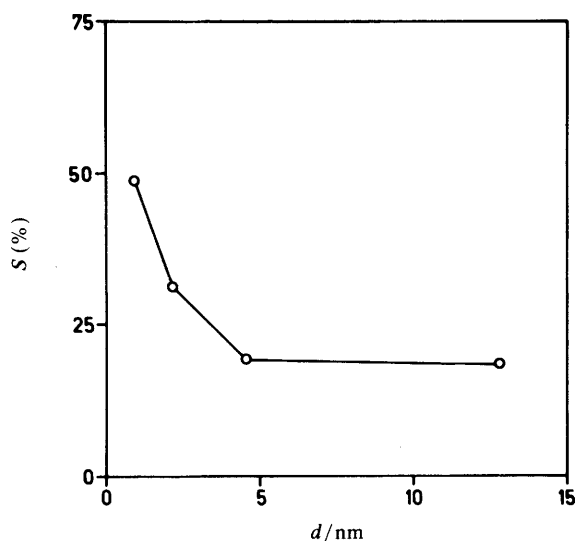


Fig. 6. Variation of the selectivity to ethene formation of reactions with $C_2H_2-H_2$ mixtures, as a function of Ir particle size.

intermediates (multiply bound or formed by dissociative adsorption of ethyne or ethene) on the surface which would lead to a non-selective hydrogenation up to ethane, would be suppressed by alloying or by diminishing the particle size (the latter is known to suppress the formation of multiply bound species).¹⁴ However, Pd was expected to be a difficult system for which to find evidence by catalytic measurements since the selectivity with this metal is already high. With pure Pd without modifications the selectivity is nearing 100%. However, iridium, which intrinsically has a very low selectivity¹⁵ offers more scope for observing selectivity changes caused by catalyst manipulation, therefore we have started with that metal.

The effect of forming bimetallics (alloying) of Ir with Cu or Au is quite pronounced. A higher selectivity than with pure Ir is observed under comparable conditions with both bimetallic systems (fig. 5). Selectivity to ethene also depends on the particle size of Ir. Smaller particles are more selective to ethene, as seen in fig. 6.

As expected, it was more difficult to arrive at clear-cut conclusions with Pd.¹⁶ In the static system used by us the final selectivity with Pd is not reached immediately, but is a function of conversion. In the first stages of reaction more C_4 and C_6 hydrocarbons are formed than in the latter stages, and the selectivity to ethene (related to the total C_2 hydrocarbon production) increases in the course of the reaction. Only at the end of the repeated run (with the same surface) does the selectivity to ethene level off. This final selectivity shows very little variation with the particle size.

Two other metals were also studied as far as the variations of the selectivity with particle size are concerned. Rhodium behaves like Ir, but the variations are less pronounced than with Ir,¹⁷ and Pt resembles Pd.¹⁶

Discussion

It is generally accepted¹⁸ that a fraction of ethane is formed from ethyne by a consecutive reaction in which weakly adsorbed ethene plays the role as an intermediate. Ethene can be displaced from the surface by ethyne, which is more strongly adsorbed than

ethene. This is the so-called thermodynamic factor in controlling the selectivity to ethene. The step underlying this mechanism, the displacement of molecularly adsorbed ethene by ethyne, can be seen by vibrational spectra, as mentioned above.

Alloying of Pd with Cu makes the formation of multiply bound ethylidyne from molecularly bound precursors (C_2H_2 , C_2H_4) slightly more difficult (fig. 1 and 2). Other results presented above show that oxygen or carbonaceous (hydrogen-lean) layers make the formation of the triply bound ethylidyne more difficult too, whereas formation of the doubly bound ethylidene is less negatively affected, or is even promoted. This strongly suggests that multiple bonding or any dissociative adsorption (C—H dissociation) can be influenced by blocking, i.e. it is regulated by the available ensemble size. Moreover, it is feasible to conclude that the higher the multiplicity of bonding between the adsorbate and the metal and the higher the degree of dehydrogenation of the species, the more important is the ensemble size effect in the formation of these species.

Let us now turn our attention to the catalytic data. A modification of the surface by a metal which itself is not active (Au) or by a metal which has a low activity but a high selectivity to ethene (Cu), increases S (ethene) considerably. Both Cu and Au are known to be very poor at breaking C—H bonds.¹⁸

It is known from our previous work that decreasing the particle size suppresses the formation of species multiply bound to the metal surface.¹⁴ In compliance with this, S (ethene) for Ir catalysts is enhanced when the metal particle size of Ir is diminished.

By combining the information on adsorption and hydrogenation reactions obtained here and in the literature²⁰ a conclusion can be formulated: the non-selective hydrogenation of ethyne to ethane proceeds *via* multiply bound (e.g. ethylidyne and ethylidene) and possibly dissociatively adsorbed ($-C\equiv CH$) species. The formation of these species can be controlled by the ensemble size effects. At the moment, a more detailed description cannot be suggested since it is not known whether the splitting in the pathways (ethene *vs.* ethane) occurs at the stage of ethyne adsorption or ethene adsorption.

References

- 1 W. M. H. Sachtler, *Faraday Discuss. Chem. Soc.*, 1981, **72**, 7; M. W. Vogelzang, M. J. P. Botman and V. Ponec, *Faraday Discuss. Chem. Soc.*, 1981, **72**, 33.
- 2 A. S. Al-Ammer and G. Webb, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 657; L. Guzzi, R. B. la Pierre, A. H. Weiss and E. Biron, *J. Catal.*, 1979, **60**, 83.
- 3 J. W. Geus, *Dutch Patent* 6705 259 (1967).
- 4 H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy* (Academic Press, New York, 1982); L. L. Kesmodel, L. H. Dubois and G. A. Somorjai, *J. Chem. Phys.*, 1979, **70**, 2180.
- 5 B. J. Bandy, M. A. Chesters, D. I. James, G. S. McDougall, M. E. Pemble and N. Sheppard, *Philos. Trans. R. Soc. London, Ser. A*, 1986, **318**, 141.
- 6 P. Skinner, M. W. Howard, I. A. Oxtan, S. F. A. Kettle, D. B. Powell and N. Sheppard, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 1203; M. W. Howard, S. F. Kettle, I. A. Oxtan, D. B. Powell, N. Sheppard and P. Skinner, *J. Chem. Soc., Faraday Trans. 2*, **77**, 397.
- 7 J. A. Gates and L. L. Kesmodel, *J. Chem. Phys.*, 1981, **76**, 4281; E. S. Kline, Z. H. Kafafi, R. H. Hauge and J. L. Margrave, *J. Am. Chem. Soc.*, 1987, **109**, 2402.
- 8 G. D. Waddill and L. L. Kesmodel, *Phys. Rev. B*, 1985, **31**, 4940.
- 9 S. Teratani and K. Hirota, *Z. Phys. Chem. N.F.*, 1970, **69**, 271.
- 10 A. D. van Langeveld, H. A. C. M. Hendrickx and B. E. Nieuwenhuys, *Thin Solid Films*, 1983, **109**, 179.
- 11 G. H. Hatzikos and R. I. Masel, *Surf. Sci.*, 1987, **185**, 479; J. A. Gates and L. L. Kesmodel, *Surf. Sci.*, 1983, **124**, 68; N. R. M. Sassen, *Thesis* (Leiden University, 1989).
- 12 L. L. Kesmodel, G. D. Waddill and J. A. Gates, *Surf. Sci.*, 1984, **138**, 464; T. S. Marinova and K. L. Kostov, *Surf. Sci.*, 1987, **181**, 573 [see also ref. (4) and (11)].
- 13 R. Imbihl and J. E. Demuth, *Surf. Sci.*, 1986, **173**, 395; T. S. Marinova and K. L. Kostov, *Surf. Sci.*, 1987, **185**, 203; J. L. Gland, *Surf. Sci.*, 1980, **93**, 487; K. Prabhakaran, P. Sen and C. N. R. Rao, *Surf. Sci.*, 1986, **177**, L971.
- 14 E. H. van Broekhoven, J. W. F. M. Schoonhoven and V. Ponec, *Surf. Sci.*, 1985, **156**, 894.
- 15 N. Yoshida and K. Hirota, *Bull. Chem. Soc. Jpn*, 1975, **48**, 184.
- 16 M. Deng, unpublished results.

- 17 F. Jongerius, *M.Sc. Thesis* (Leiden University, 1987).
- 18 G. C. Bond, in *Catalysis by Metals* (Academic Press, London, 1962).
- 19 V. Ponec, *Adv. Catal.*, 1983, **32**, 149.
- 20 G. C. Bond, D. A. Dowden and N. MacKenzie, *Trans. Faraday Soc.*, 1958, **54**, 1537; H. Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446.

Paper 8/04782K; Received 28th November, 1988