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THE HYDROGENATION OF ACETYLENE ON SUPPORTED BIMETALLIC Pt-Ir AND Pt-Re CATALYSTS

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Hydrogenation of acetylene has been studied with a series of Pt-Re and Pt-Ir catalysts. The results supplied some information concerning the importance of the potential electronic structure (ligand) effect of alloying and on the effect of selfpoisoning.

1. Introduction

Up to now, when selectivity problems have been studied attention has usually been directed to *parallel* running, simultaneous reactions, such as for example, the network of skeletal reactions of hydrocarbons [1–3] and the reactions of synthesis gas [4–7]. It appeared that the most important effects on selectivity observed with alloys (bimetallics) are caused by the fact that one active metal is placed in a matrix of another metal and by that the average size and composition of the ensembles of active sites is varied. Changes in the electronic structure accompanying alloy formation are in general not very pronounced and their manifestation in catalysis seems to us to be rather elusive [1], although there are repeated claims of evidence for these effects [8]. The last statements imply that attention should also be turned to simultaneous *consecutive* reactions. There are several strong indications that the hydrogenation of acetylene to ethylene and ethane forms a network of parallel *and* consecutive reactions [9–11]:

acetylene ethylene ethane [scheme 1]

whereby with systems with a high selectivity to ethylene (Pd, Pt) the reaction is governed by the so called thermodynamic selectivity (i.e. essentially the heats of adsorption of acetylene and ethylene) [12]. A more systematic search for factors determining the selectivity in reactions of acetylene (electronic structure vs.

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geometrical ensemble size) has not been performed yet. The IR studies of adsorbed CO on various Pd (Cu and Ag) and Pt alloys (Cu, Re and Sn) did not reveal any pronounced electronic structure (or ligand) effect of alloying [13–15] but one could argue that CO is not a proper probe to detect potential effects on, say, acetylene hydrogenation. Therefore, additional experiments in this direction are justified. Effect of alloying on the acetylene hydrogenation have already been established with some systems: Ir/Cu, Ir/Au [16] and earlier literature data exist on Pd/Au, Pd/Ag [17,18] and Ni/Cu [12]. It is common to the just mentioned systems that the Ib metals are much less active than the indicated transition metal. In experiments under static conditions, the selectivity to ethylene increases marginally [17] or, in some other cases, markedly [18]. As far as the potential electronic structure effects on catalysis are concerned, the Ib metals are in the periodic table to the right of the transition metals. It seemed then interesting to compare the behaviour of an VIII-Ib alloy with an alloy of Pt with a metal positioned to the left of the metal in question in the periodic table. The alloys Pt-Re and Pt-Ir belong to the last mentioned category. If the electronic structure effect were the prevailing factor in establishing the selectivity of the bimetallic system, one would expect the same type of change in the activity and the selectivity, for both the Re and Ir alloys of Pt. Of course, a complicating factor with the Pt/Ir bimetallics is the fact that Ir itself is active in the hydrogenation of acetylene (showing a rather low selectivity), but this does not prevent to see possible selectivity effects.

Not only the electronic structure effects and the ensemble size effects of alloying have to be considered in speculations concerning the acetylene hydrogenation but also the effects of alloying on the formation and properties of the carbonaceous layer. Such layer is always formed on the surface of working catalysts and some authors suggest that this layer is even the main place where both the acetylene and ethylene hydrogenation take place [11] and some others assume that this is true for at least the hydrogenation of acetylene [19,20]. According to the information obtained with skeletal reactions of hydrocarbons on Pt-Ir and Pt-Re alloys [21] (bimetallics), the formation of the deposited carbonaceous layer is influenced in the mixed metal system and, if the layer has, indeed, a crucial role in the acetylene (or ethylene) hydrogenation (as suggested) one would expect selectivity and activity effects induced by alloying. However, in this case indirectly, through the formation of the carbonaceous layer.

2. Experimental

All catalysts were prepared by a classical wet impregnation, the metal precursors used were $H_2Pt(OH)_6$ and $(NH_4)_2IrCl_6$ and Re powder, as supplied by Johnson Matthey. The metal salts were dissolved in aqua regia, after this the acid was evaporated and water added. The support used was SiO_2-Kieselgel (Merck, 480 m^2/g). After the impregnation the catalysts were dried overnight at 110 °C, calcined in oxygen at 250 °C (3 h) and reduced ex situ at 400 °C (5 h). The catalysts were reduced in situ at 400 °C for 5 hours. The degree of the total reduction has been discussed [22].

The hydrogenation reaction was studied in a static high vacuum system with a background pressure better than 5×10^{-6} Torr with the catalyst in situ. The reaction mixture consisted of acetylene and hydrogen ($C_2H_2/H_2 = 0.3$) with a total pressure of about 0.7 Torr. The products were analysed through a continuous leak by means of a mass spectrometer. The peaks at $m/e = 30$, 27 and 26 were used to determine the ratios of ethane, ethylene and acetylene respectively whilst the whole fragmentation pattern was used to check the reliability of the analysis.

The selectivity to ethylene S is defined as:

$$S = \mathrm{p(ethylene)}/\{\mathrm{p(ethylene)} + \mathrm{p(ethane)}\} \times 100\%.$$

The activity is defined as:

$$\alpha_9 = \frac{\mathrm{p(ethylene)} + \mathrm{p(ethane)}}{\mathrm{p(ethylene)} + \mathrm{p(ethane)} + \mathrm{p(acetylene)}} \times 1/\mathrm{g(M)}$$

For the determination of the activity (α_9) the partial pressures are determined nine minutes after the reaction has been started. The α_9 is evaluated per gram active metal. Finally, during the hydrogenation reaction some oligomerization is always found. The mass spectrometry used in this study did not allow to determine the exact composition of the polymers but GC analysis showed that they consist mainly of C_4 and C_6 products. The oligomerization selectivity, S^*(olig.) is defined as:

$$S^*(\mathrm{olig.}) = I(\mathrm{olig})/\{I(\mathrm{C=C}) + I(\mathrm{C-C}) + I(\mathrm{olig.}) + I(\mathrm{benzene})\} \times 100\%,$$

where I(product) refers to the total peak intensity of the fragmentation pattern of the product in question. Since the exact composition of the oligomerization products is not known it is not possible to calculate the selectivity quantitatively. The above defined selectivity to oligomerization should only be used in a comparative, qualitative way.

3. Results

The Pt bimetallic catalysts were characterized by CO adsorption and Electron Microscopy and the results of the characterization are presented in table 1. For the sake of completeness also the chemisorption data concerning Pt-Re catalysts are presented although it is not clear how these results should be evaluated. It is not known whether CO adsorption does occur on Re in Pt-Re system (pure Re does not adsorb CO in the apparatus used) and when it does, it is unclear what the stoichiometry of adsorption is. XRD showed very low peaks with the Pt/Ir catalysts, resulting from the low fraction of metal particles larger than 3 nm. The results of the determination of the particle size are presented in fig. 1 for two catalysts. The other catalysts measured show a similar particle size distribution. The results of the catalytic experiments for Pt-Re at 100 ° C are presented in fig. 2. With only 25% Re added to Pt, the activity per gram Pt decreases strongly and an additional increase in the Re content results in a further decrease of activity at Re concentrations higher than 50%. Activity (α_9) per unit CO adsorption decreased by a factor of up to 5 with 75% Re. The 100% Re catalyst is not active at all, even at 200 ° C. The reaction temperature that has been chosen to study the Pt-Re system is quite high but this is necessary since the catalysts with higher Re content show a very low activity. The effect of the increasing temperature on the selectivity has been shown, by previous work [12,21], to be positive with regard to the selectivity to ethylene. Figure 2 shows that the addition of Re has only a limited but a positive effect on the selectivity to ethylene. In fig. 3 the results for the Pt-Ir catalysts are presented (in this case the data are for room temperature). One can see that addition of Ir has a rather small effect on the selectivity to ethylene. Only the 100% Ir shows a low selectivity to ethylene, and this is the usual behaviour of this metal [12]. Besides hydrogenation to ethane and ethylene, oligomerization was observed. In fig. 4 the selectivity to oligomerization is plotted. Although this selectivity remains always low, a gradual increase is observed with increasing Pt content. The activity (also plotted in fig. 4) shows a broad scatter, but it is clear that the Pt containing catalysts are all more active

Table 1
Characterization of the catalysts used

cat. [+]	%Pt	*d* (nm, EM)	D (%) *
Pt1	100	1.6	44
PtIr31	75	1.7	48
PtIr11	50	1.8	51
PtIr13	25	1.5	80
PtIr15	16.7	n.d.	74
Ir1	0	1.6	46
Ir2	0	n.d.	41
PtRe31	75	2.0 [0]	21
PtRe11	43.5	2.0	23
PtRe13	25.6	2.0	8
PtRe18	11.5	n.d.	5

[+] Code refers to the ratio of the metals used.

* Dispersion determined by measurements in flow of gases (H_2/CO) (quantasorb) with EUROPt-1 as a reference compound [29].

[0] Catalyst contains also a fraction of particles of about 3.8 nm which is also determined by XRD (3.3 nm).

n.d. not determined.

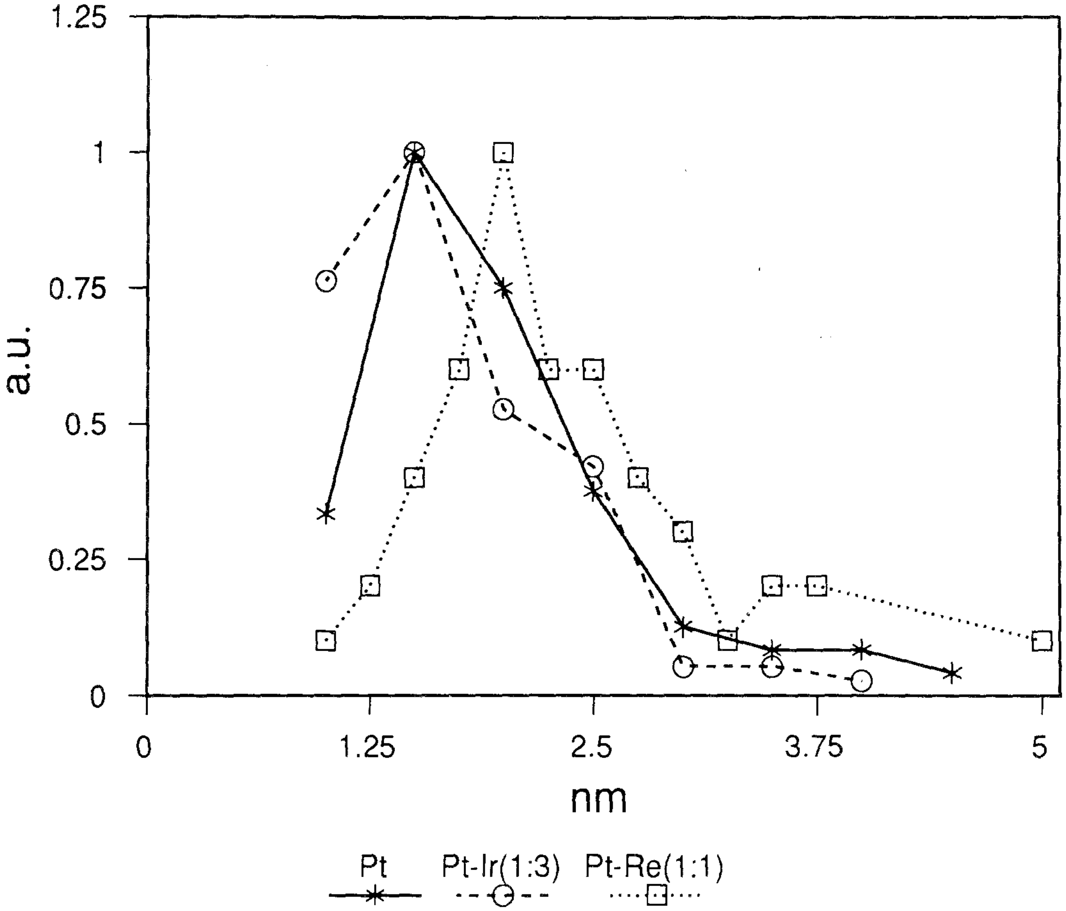

Fig. 1. Particle size distribution for a Pt and a Pt-Ir(1 : 3) catalyst. The frequency values are normalized to unity for the most frequency found particle size, ★———★ = Pt, ○– – –○ = Pt-Ir (1 : 3), □· · · · ·□ = Pt-Re (1 : 1).

than the pure Ir catalyst. In order to reveal possible effects of the deposition of a carbonaceous layer, two measurements in sequence have been performed with the same catalyst. In such experiment the gas mixture is pumped off after each run. This is known to result in a dehydrogenation of the adsorbed species [24] and thus in a more extensive formation of the carbonaceous layer than upon the reaction proper; the second catalytic run on the same surface can thus reveal possible effects of such layer. It appeared that when the Pt and Pt bimetallic catalysts were studied in this way (with both Ir and Re), no effect on the selectivity was observed. The activity of the catalysts was suppressed by the treatment by about a factor 2 between the first and second run but the selectivity stayed the same.

4. Discussion

Both addition of Re and of Ir to Pt results in a decrease in the activity (per unit weight of the metal) of the hydrogenation of acetylene compared with the pure Pt catalysts. The activity taken per unit CO adsorption is almost constant with Pt-Ir alloys in a broad composition range, only pure Ir is less active. The activity per unit adsorbed CO decreases with Pt/Re catalysts, pure Re is completely inactive. This means that the Pt bimetallics behave in a similar manner like the bimetallics of a transition metal with an inactive group Ib metal [16,17]. Such a similarity in the results would not be expected if that what is called by the literature an electronic structure effect were the decisive factor in establishing the resulting activity of the catalysts. Obviously, one has to look for another explanation.

Rhenium is a metal which otherwise interacts actively with saturated hydro-

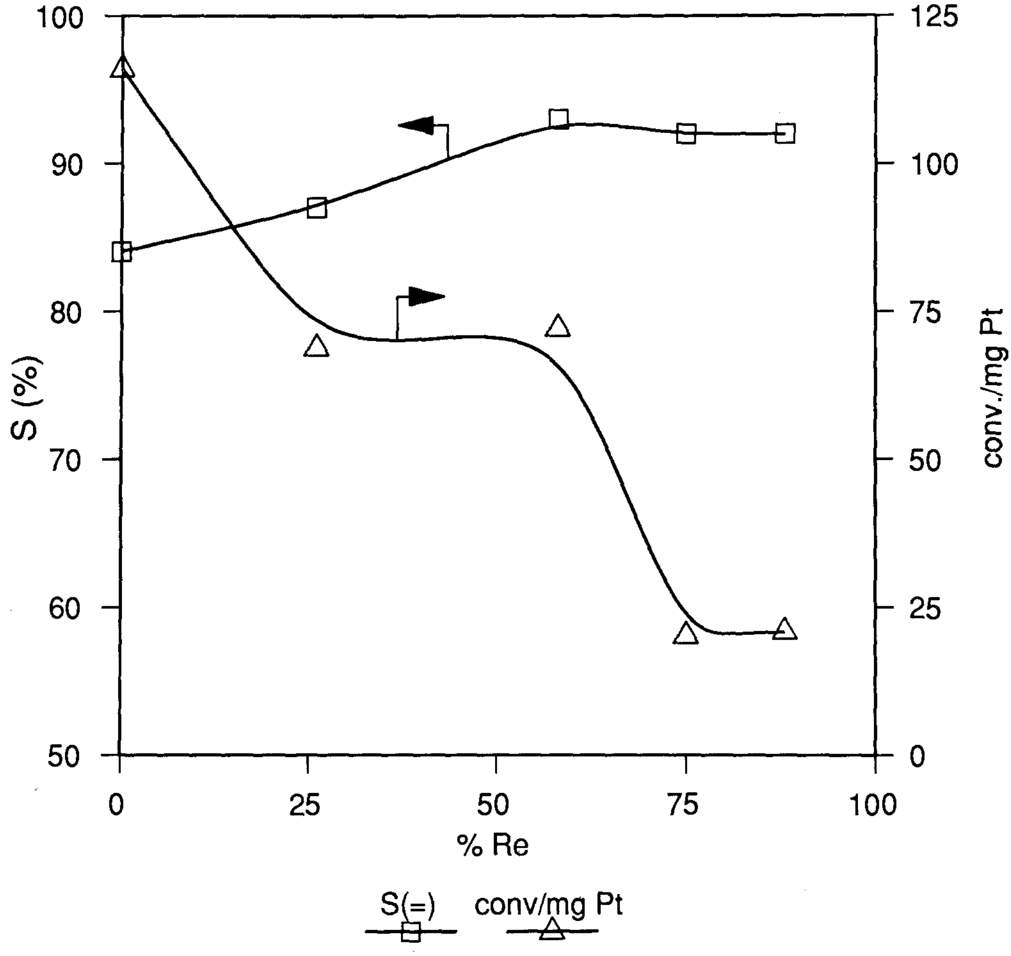

Fig. 2. Activity and selectivity in the hydrogenation of acetylene on Pt-Re catalysts as functions of the Re content, △——△ = activity per gram Pt, □——□ = selectivity to ethylene.

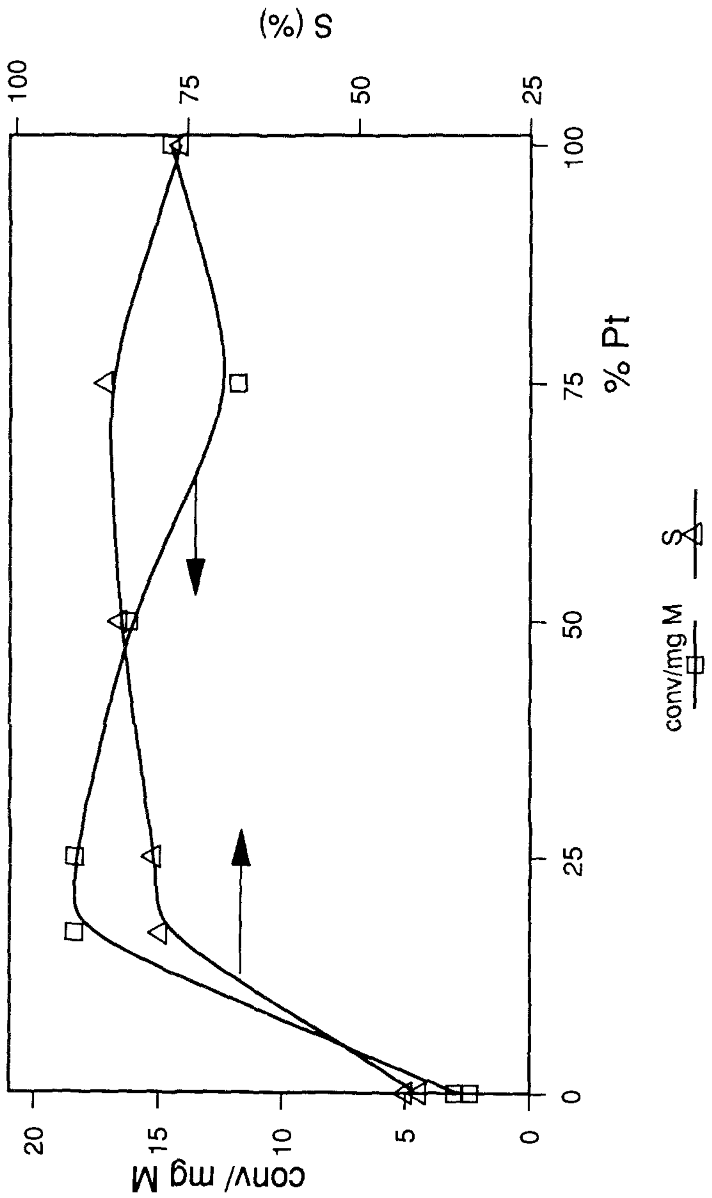

Fig. 3. Selectivity to ethylene and activity for Pt-Ir catalysts as function of the Pt content □——□ = activity per g M, △——△ = selectivity to ethylene (the lines have no other meaning than to interconnect corresponding points).

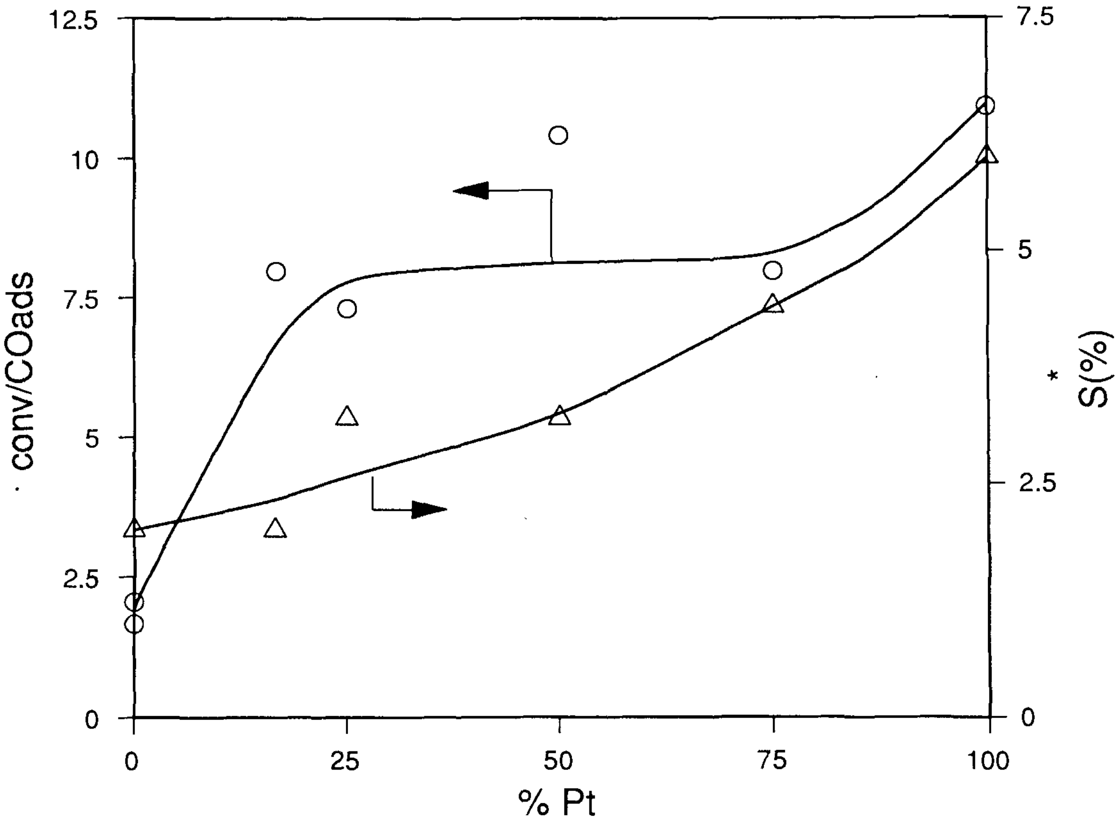

Fig. 4. Activity and selectivity to oligomerization products as functions of the Pt content for the Pt-Ir catalysts, ○——○ = activity per adsorbed CO, △——△ = selectivity S^* to oligomerization (see text for the definition of S^*).

carbons and induces in the steady state mainly the C–C bond splitting reactions (the so called 2C $\alpha\beta$ splitting) [22]. In the hydrogenation of acetylene, Re is inactive even at temperatures as high as 200 ° C. We infer that this is because Re binds acetylene or its fragments too strongly. Haining et al. [23] published data that support the idea that indeed a hydrocarbon or its fragments are more strongly bound to Re than to Pt. In such a situation one might expect that atoms of Re, inactivated by strongly adsorbed species should modify the surface of the transition metal (Pt) in the same sense as a group Ib metal does, at least as far as the influence on the ensemble size is concerned. When the trend in the selectivity data is considered, the conclusion reached in the foregoing paragraph concerning the electronic effect is corroborated: the selectivity to ethylene is increased by the addition of Re as is for example the selectivity of Ir after addition of a Ib metal. Since the potential selectivity effect of the Re addition to Pt is rather small, an Ir/Re catalyst (1 : 1) has been tested. Again the results remind strongly of Ir/Au and Ir/Cu catalysts. A decrease in activity and an increase in the selectivity to ethylene is observed (determined at 100 ° C, Ir: $S = 65\%$, Ir/Re: $S = 80\%$, α_9 is 5.1 and 2.8 respectively (per gram Ir)). Whereas an explanation based on the assumed operation of an electronic effect does not seem to be possible, all available data can be explained selfconsistently if one assumes that the activity and selectivity are related to the properties of the individual alloy components and these properties are not more than marginally influenced by the formation of the bimetallic system.

A suitable model to discuss the results of the hydrogenation of acetylene is a model wherein two separate pathways are important (see scheme 1): One pathway results in the primary hydrogenation to ethylene and the other in the direct hydrogenation to ethane [9–11]. Ethylene formed by the first pathway does not react further to ethane (although this reaction is fast and is thermodynamically favoured) as long as acetylene is still present in the reaction mixture. It is reasonable to expect that the deep dehydrogenation in the adsorbed state leading the reaction to ethane is related to a multi site adsorption of acetylene which might moreover be accompanied by C–H bond dissociation. Such an adsorption would be suppressed by addition of an inactive component like Cu or Au. Indications that this effect might be important have been presented in a paper by Sassen et al. [24]. A similar effect would than be expected if Re is added to the Pt (or Ir) catalysts and becomes covered by firmly bound species and modifies by that the active metal (Pt or Ir) surface (less of large ensembles) and thus increases the selectivity to ethylene.

During the investigations just described, no information was obtained on the surface composition of the Pt-Ir and Pt-Re alloys. There are some data on the Pt-Ir system by Kuyers and Ponec and these data show a strong enrichment in Pt for bulk alloys [25].

However, this enrichment in Pt will be less with the small particles, such as used in this study [26]. The Pt enrichment would result in a strong effect on the selectivity even when only small amounts of Pt are added to the Ir, which is indeed found under the experimental conditions used in this study.

Although we have discussed above two effects that we expected to be the potential source of the variations in activity and selectivity due to alloying, the electronic effect and the effects resulting from multi site adsorption of the intermediate leading to ethane, there is still a third idea which can be found in the literature: hydrogenation is assumed to take place not on the metal but on the carbonaceous layers that are deposited on the metal in the first stages of the reaction [11,19,20]. In order to check whether such an effect could be important with the Pt catalysts, sequential experiments have been performed (see above). The treatment applied resulted indeed in a decrease in the activity, which indicates that some carbonaceous deposits were formed on the catalysts. However, the selectivity to ethylene remained more or less unchanged. If an active or a selectivity modifying carbonaceous layer were formed, opposite effects on the activity and/or changes in the selectivity are expected to occur (the latter effect, an improvement of the selectivity in a sequential experiment was, indeed, found for Pd catalysts [21]). We suggest that in the case of Pt the carbonaceous deposits play if any only a minor role in the hydrogenation of acetylene.

In the literature some papers can be found that consider the presence of dissolved or 'occluded hydrogen' as the factor responsible for the low selectivity whenever found in the hydrogenation of acetylene [27]. The metal that one would expect to be most affected by dissolution would be Pd. However, under the conditions used, even for Pd the stoichiometry for the Pd hydride is only $PdH_{0.0055}$ [28]. For this reason we rejected this line of thought in an earlier paper [21] and we expect an even lower influence of 'dissolved hydrogen' in the catalysts studied here. The highest occlusion of H_2 is claimed [27] to occur on Ir. This claim cannot be accepted without doubts (the method used to establish the extent of occlusion determines actually the extent of H_2/D_2 exchange with all hydrogen in the catalyst, not only with the occluded hydrogen) but also when we accept it, we do not see it operating here: even a high concentration of Ir (occluding H_2) in Pt does not suppress the selectivity of Pt.

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