Catalysis Letters 8 (1991) 263–268

THE HYDROGENATION OF ACETYLENE IN A PULSED SYSTEM OVER Ni AND Ir CATALYSTS

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Received 16 August 1990; Accepted 10 January 1991

In order to detect possible effects of deposited carbonaceous layers on the hydrogenation of acetylene, a pulse flow reactor was used to study this reaction. Silica supported Ni and Ir catalysts were used to study the effect of variations in the particle size and of combining the active metal with an inactive component (Au).

Keywords: Acetylene, hydrogenation, Ni, Ir

1. Introduction

The hydrogenation of acetylene is usually considered to proceed through two separated pathways [1–3]. The first reaction pathway is a direct hydrogenation to ethane upon one sojourn on the surface, the second pathway is a two-step reaction in which in the initial step ethylene is formed and in the final step molecular ethylene is further hydrogenated to ethane. The final step in the second pathway is often assumed to be of minor importance due to the thermodynamic factor: ethylene is displaced from the surface by acetylene before the final step in the reaction can occur [4]. In the literature the intermediates of the reaction are sometimes considered to be adsorbed on or transported by a carbonaceous layer [3,5,6]. Furthermore, it is known that variations in the particle size of the supported metal particles and alloying of the metal with a second, less active metal, can result in variations in both the selectivity to ethylene [6–8], and the deposition of carbonaceous layers [9,10]. To study the effect of deposited carbonaceous layers on the hydrogenation of acetylene, the reaction was performed in a pulse flow reactor. The metals used in this study are iridium and nickel. Apart from variations in the metal particle size, also the effect of bimetallics formation of the two metals with gold has been checked. With both variations, the effect on the selectivity to ethylene and the effect on the deposition of carbon is examined.

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2. Experimental

Precursors used to prepare the catalysts were $Ni(NO_3)_2$, $IrCl_3$ and Au (dissolved in aqua regia). Particle size variations were induced by variations in catalyst preparation. Large particle catalysts were prepared by mechanically mixing the precursor salt with the support. The small particle catalysts were prepared by coimpregnation (with Ni catalysts) or homogeneous precipitation (with Ir catalysts) [11]. Due to the high activity of the catalysts, low metal loadings were used, in the order of 0.1% by weight, to keep the conversion at suitable temperatures as low as possible. From previous experiments it is known that the preparation methods used except mechanically mixing, combined with a low metal loading, result in a small metal particle catalyst. However, the low loading and high dispersion made an exact characterization of some of the catalysts by transmission electron microscopy, CO adsorption or X-ray diffraction unfeasable. The pulse flow apparatus was used at a background pressure of 1.8 bar. Hydrogen was used as carrier gas and the gas mixture was analyzed by G.C. Pulses containing 50 μl of the reaction mixture ($C_2H_2 : H_2 = 1:2$) were passed over the catalyst.

The selectivity to ethylene is defined as:

$$S(C=C) = (C=C/(C=C+C-C)) \times 100\%. \tag{1}$$

At low conversions only ethane and ethylene are observed as products. At high conversions some butanes and hexanes are also found.

3. Results

In table 1 the results for the Ni and Ir catalysts are summarized.

The overall conversion achieved with catalysts the selectivities of which have to be compared must be kept as low as possible. Usually it is kept below 10%, to

Table 1

Catalyst	M [c] (%)	d [a] (nm)	T(°C)	α [b]	$S_l(C=C)$ [b]	$S_u(C=C)$ [b]
Ni	0.1	s	22	4	82	82
Ni	0.1	l	22	6	58	67
Ni/Au 1:1	0.2	–	22	4	80	80
Ir	0.1	s	80	2	63	80
Ir	0.56	26	0	2	53	71
Ir	0.56	26	65	38	22	36
Ir/Au 2.2:1	1	20	65	9	66	66

[a] s = small, l = large.

[b] α, S_l: fresh catalyst; S_u: used catalyst.

[c] wt.% Ir or Ni.

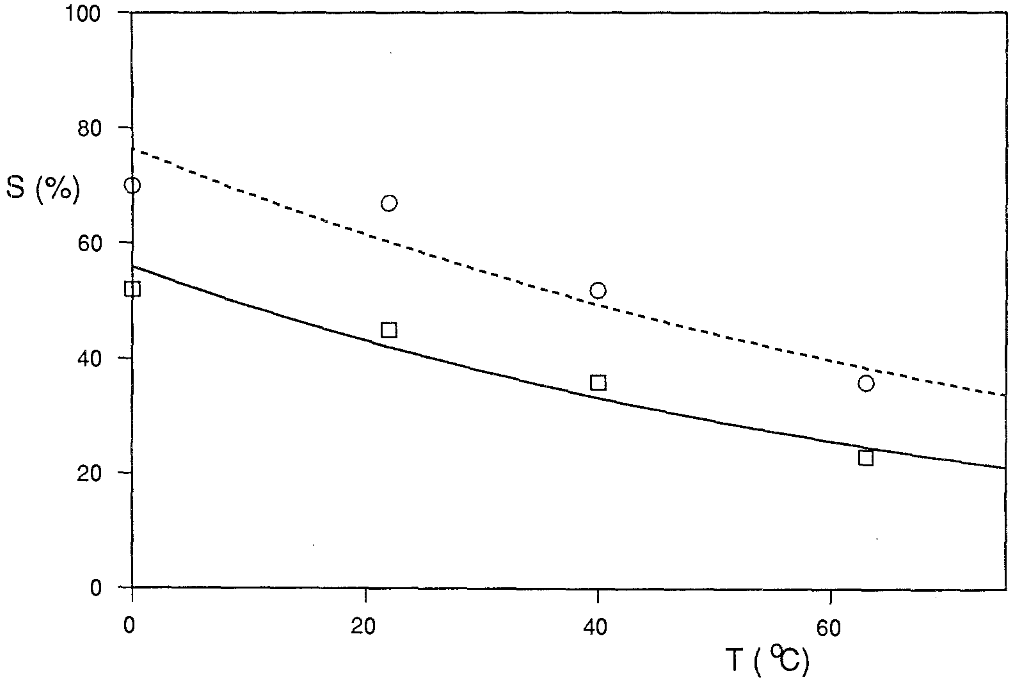

Fig. 1. The selectivity to ethylene for a small (○) and a large (□) particle Ir catalyst as functions of the reaction temperature.

minimize the consecutive reactions. Increasing conversion results in a decreasing selectivity towards ethylene, due to secondary hydrogenation to ethane.

When the Ni catalysts from table 1 are considered, it appears that at low conversions the catalyst containing small metal particles shows a higher selectivity towards ethylene than that of the catalyst containing large metal particles. Also, the selectivity of the "small particle catalyst" remains constant when more pulses of the reaction mixture are subsequently led over the catalyst. However, the large particle catalyst does show a different selectivity for the used and the fresh catalysts. The used catalyst is more selective to ethylene.

When Ni is combined with Au, the activity decreases (with a Ni loading twice as high, the activity is similar) which indicates that Ni and Au are in some kind of contact. Again, the selectivity of the bimetallic catalyst is higher and not influenced by aging of the catalyst.

Similar variations, although not as pronounced as found with Ni, are observed with the Ir catalysts. The selectivity to ethylene increases when the metal particle size decreases (see fig. 1).

When the large particle, pure Ir catalyst is compared with the Ir/Au catalyst it is again found that the bimetallic catalyst shows a higher selectivity to ethylene. When the used Ir catalysts are compared with the fresh ones, similar differences

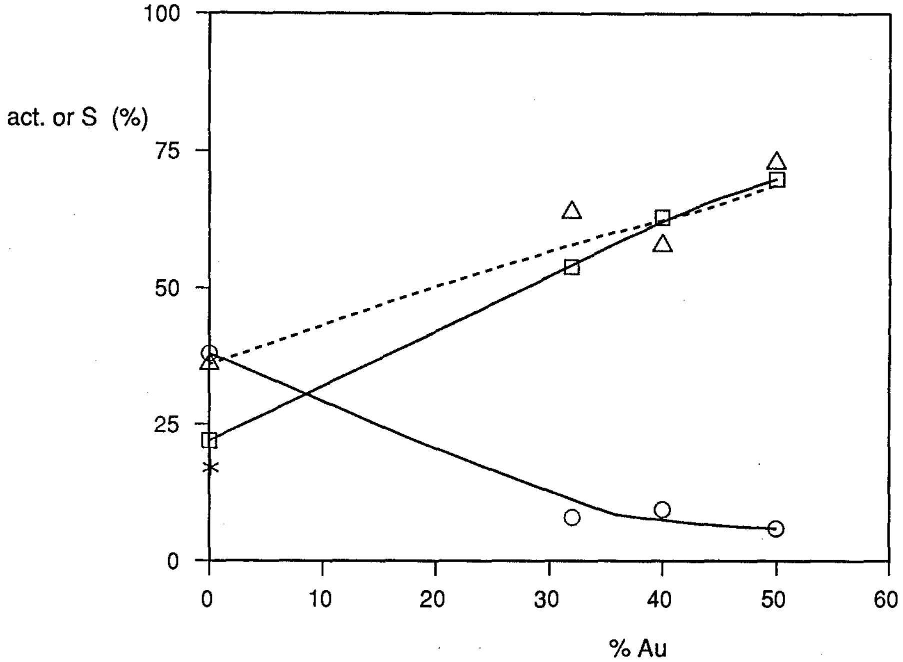

Fig. 2. The selectivity to ethylene and the activity as function of the Au content of Ir/Au catalysts ($T = 65\,°C$). □ = $S_{(C=C)}$ fresh catalyst, △ = $S_{(C=C)}$ used catalyst, ○ = activity fresh catalyst, * = activity used catalyst (only plotted for the 100% catalyst, with the other catalysts no or very minor variations with the fresh catalyst were observed).

are found as with the Ni catalysts. The large particle catalyst and with iridium also the small particle catalyst show an increase in the selectivity when more pulses of the reaction mixture have been led over the catalyst. With the bimetallic Ir/Au catalysts only small variations resulting from variations induced by the reaction mixture, if any, are observed. This is demonstrated in fig. 2.

Although with Ir and Ni catalysts variations in activity and selectivity between fresh and used catalysts have been observed in some cases, it was not possible to determine exactly the amount of carbonaceous deposits, the absolute amounts of carbon retained by the catalysts were too low to be determined quantitatively by the methods available.

4. Discussion

The hydrogenation of acetylene is usually assumed to operate by means of two separate pathways, one leading directly to ethane, the other leading to ethane via the formation of ethylene [1–3]. The actual intermediates and the active sites of these reactions are still not known. Concerning the active site, there is still discussion whether the metal is the active site or the layer of carbonaceous deposits. Recent papers arrived at a conclusion that the metal itself is the active component of the catalyst and variations in the metal function are directly reflected in the selectivity and activity of the catalyst [6–9]. Both "alloying" with less active or inactive metals, or decreasing the average metal particle size lead to an increase in the selectivity to ethylene. In the publications quoted above and elsewhere (see e.g. [5]), this was explained by assuming that the direct hydrogenation to ethane proceeds by means of an intermediate that requires ensembles of active metal atoms rather than single atoms, in contrast to the hydrogenation to ethylene. In order to study the effect of the gradual deposition of "carbon" more closely, the experiments described above have been performed. When we examined the results of the fresh catalysts, it appeared that all trends found in the low pressure static system can again be observed in the pulse flow system operating at higher pressures. For example, decreasing the particle size and "alloying" with an inactive metal do both result in an increase in the selectivity to ethylene. Although the experimental system allows in principle determination of the amount of carbon retained by the catalyst, no carbon deposition could be detected, which means that at pressures used only small amounts of carbon are retained on the catalysts. Still, when several pulses of the reaction mixture have been passed over the catalysts, then in some cases (pure Ir and the large particle Ni catalyst) the selectivity of the used catalyst is different from that of the fresh catalyst. When an effect is observed, the final selectivity is always higher, whereas the activity decreases or remains more or less constant. The effect of the particle size variation and of alloying are in accordance with the above mentioned idea that the direct hydrogenation to ethane requires metal atom ensembles. The shift in selectivity as function of the "time on stream" does not contradict this conclusion. Rather, we would expect an effect as found here when some carbon is retained. Small amounts of "carbon" can act in a similar manner as alloying with for example Au, i.e. by diluting the active metal atoms and decreasing the average ensemble size. Deposition would then result in an increase in the selectivity to ethylene. However, if the carbonaceous layers were active, and/or represent the selectivity determining phase, as some authors speculate on, more pronounced effects would be expected on the activity and selectivity when the layer has been deposited. Furthermore, the very low extent of carbon deposition contradicts the proposed role of the carbonaceous layers, as the locus of the catalytic activity. This is true at least for the metals studied here.

Acknowledgement

The $IrCl_3$ used in this study was kindly supplied as a loan by Johnson Matthey.

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