Catalysis Letters 4 (1990) 37–42

HYDROGENATION OF BUT-1-YNE ON PLATINUM CATALYST: ROLE OF REVERSIBLE ADSORBED HYDROCARBON DEPOSIT

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Received 11 July 1989; revised 31 October 1989

By using rectangular pulses of but-1-yne carried by H_2 or H_2-He mixtures over a platinum catalyst, it was possible to visualize the build-up of an adsorbed hydrocarbon deposit which is a necessary condition for getting a selective catalyst (on platinum, but-1-ene selectivity is 90%). Such a deposit is reversibly adsorbed since it desorbs as hydrogenated butyne molecules when the butyne pressure drops at the end of the pulse. Moreover it was shown, during stationary phase, that the sudden fall in the selectivity at high but-1-yne conversion, is due to the desorption of such reversibly adsorbed molecules.

1. Introduction

Numerous studies have been devoted to the optimization of palladium catalysts for the semi-hydrogenation of acetylenic compounds: the changes of experimental conditions, the effects of the metal particle size, the addition of other compounds, either to the catalyst or to the hydrocarbon charge, were studied [1 and references therein]. In such works, in order to conclude about the efficiency of any change, it is necessary to compare the activities and selectivities in the reactions by varying a single factor at the same time. This is difficult on palladium due to the very high activity and selectivity of this metal for this reaction. Platinum is known to be less active and selective than palladium in the hydrogenation of acetylenic compounds [2,3]. Therefore it is easier to vary the experimental conditions in a large scale and to conclude about the influence of any factor. So, we have studied the hydrogenation of but-1-yne on platinum.

In this paper, we focus our attention on reversible hydrocarbon deposits which were already invoked on palladium [4] but which are easier to analyze on platinum.

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2. Experimental

The catalyst was made of Pt/Al_2O_3, 0.53% weight, 42% dispersion, 200–400 μ sieved. It was prepared and characterized at the Institut Français du Pétrole, Rueil Malmaison, as described elsewhere [3]. Before each catalytic experiment, the catalyst was activated under H_2 flow at atmospheric pressure, 573 K, for one hour. But-1-yne (Air Liquide, 95% purity) was purified from acetylene impurity just before each run by distillation at low temperature (< 210 K).

Hydrogen or hydrogen-helium mixture from Air Liquide were used after purification by passing through a Pt/Al_2O_3 catalyst heated at 453 K followed by a trap at 196 K. The catalytic reaction was carried out in a glass flow system including a reactor operating under differential conditions at atmospheric pressure. After catalytic activation and cooling down to the reaction temperature (255 K–293 K), a known quantity of but-1-yne, at constant hydrocarbon pressure, was carried out along the catalyst by H_2 or H_2-He flow. The hydrocarbon pressures were obtaining knowing the vapor pressure of but-1-yne at different low temperatures, 210 K (14.2 Torr), 188 K (2.6 Torr), 183 K (1.5 Torr), 178 K (0.8 Torr). Two katharometers were inserted upstream and downstream with respect to the reactor; their signals represented the hydrocarbon pressure as a function of time. Small amounts of product were drawn off the line after the reaction at different times during the catalytic run and analyzed by gas-liquid chromatography on a 2.5 m l., 3.175×10^{-3} m o.d. dimethyl sulfolane column operating at 293 K with a flame ionization detector. In this reaction, the but-1-ene selectivity (S) was defined as the ratio, but-1-ene to but-1-ene plus butane; the but-2-enes were not detected. The conversion (Cv) was the ratio, but-1-ene plus butane to but-1-ene plus butane plus but-1-yne.

3. Results

In fig. 1, two katharometer signals are reported. The upper one was obtained after a catalytic run performed at *constant flow*, on 50 mg Pt/Al_2O_3 and the lower one was got by using 50 mg Al_2O_3 and keeping constant the other experimental conditions. By comparison, one can see two characteristics due to the metal particles: an adsorption process when the hydrocarbon was being introduced into the reactor and a desorption process after the hydrocarbon flow was stopped, hydrogen being permanently passed over the catalyst.

Let us analyze the product distributions during these runs. Al_2O_3 was found totally inactive, whereas three different phases could be distinguished with Pt/Al_2O_3:

– an initial transient phase where the but-1-yne conversion decreased and the but-1-ene selectivity increased during the adsorption process.

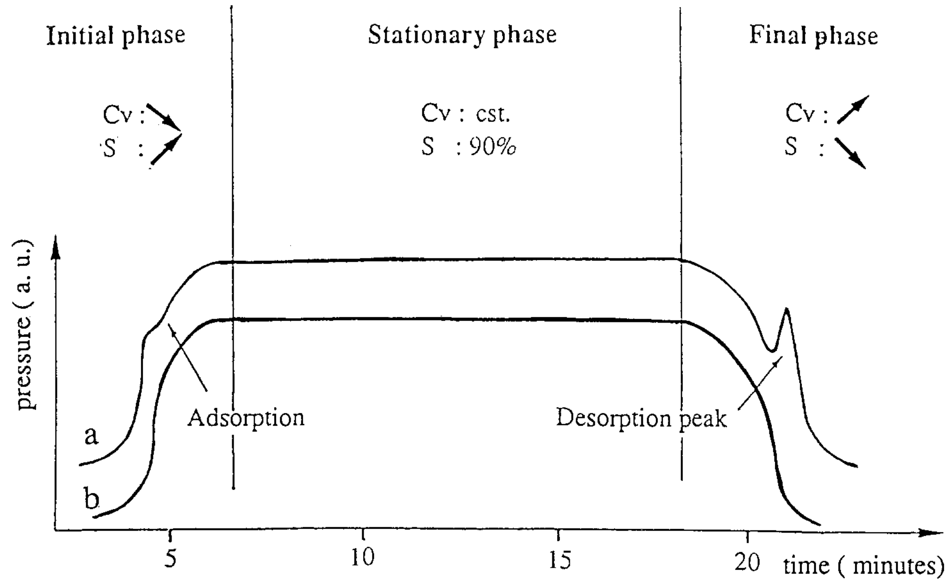

Fig. 1. Katharometer signals: hydrocarbure pressure (a.u.) as a function of time (minutes), (a) on Pt/Al_2O_3, 0.45%, D = 42%; (b) on Al_2O_3. Reaction conditions: $P_{H_2} = 760$ Torr, $P_{HC} = 2.6$ Torr, $T_{reac.} = 255$ K.

– a stationary phase where the but-1-yne conversion was constant and the but-1-ene selectivity was 90%.

– a final transient phase with a desorption peak. Just before the desorption peak the selectivity was still 90% as observed during the stationary phase, and the conversion increased due to the decrease of the hydrocarbon flow. After the peak, the selectivity was zero and the conversion was very high. The desorption peak revealed only C_4 hydrocarbons (butane, but-1-ene, but-1-yne) with a higher but-1-yne conversion and a lower selectivity than observed on the stationary phase.

In fig. 2, another type of experiment was reported. The hydrocarbon was introduced into the reactor with a constant flow (F_1): as described above, we observed an initial transient phase followed by a stationary phase in which the but-1-ene selectivity reached 90%. Afterwards we decreased step by step the total gas flow: the conversion increased due to the decrease of hydrocarbon flow (F_2, F_3), but the selectivity was still constant. It should be precised that, in our apparatus, when the flow rate was changed, the P_{H_2}/P_{HC} ratio was kept constant. If we kept on decreasing the flow down to the F_4 value, the katharometer signal revealed a desorption peak: just before this peak, the conversion reached 90% with still a high selectivity (90%), while along this peak the product analysis revealed only C_4 hydrocarbons in which the percentage of butane increased rapidly to be the sole product at the end of the peak. Afterwards, if the hydrocarbon flow was kept equal or lower than $F_4(F_5)$, the butyne remained

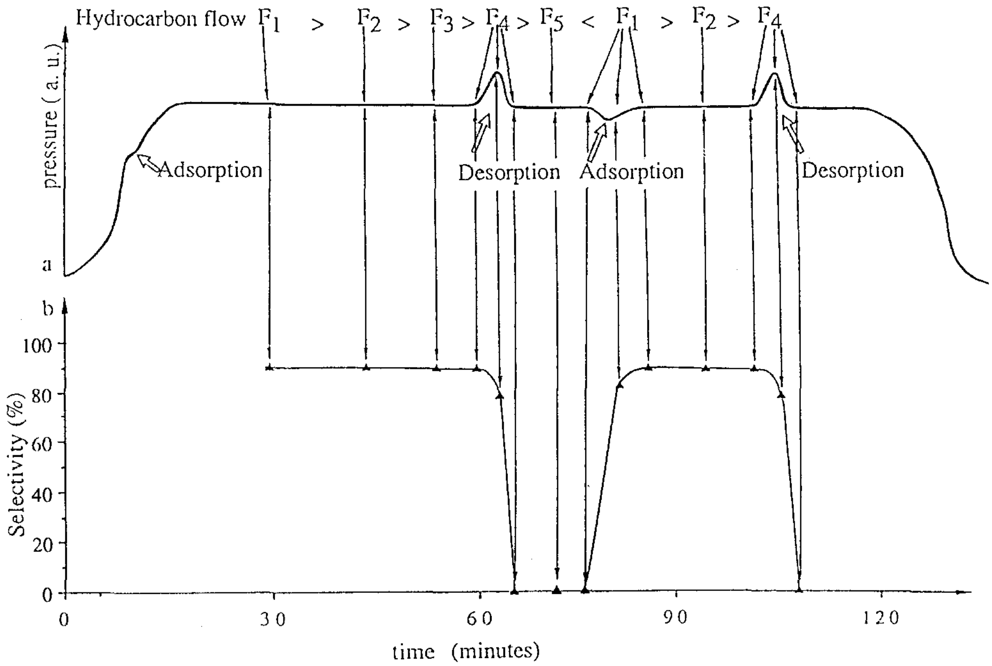

Fig. 2. But-1-yne hydrogenation on Pt/Al_2O_3, 0.45%, D = 42% in varying the hydrocarbon flow, (a) hydrocarbon pressure (u.a.) as a function of time (minutes), (katharometer signal); (b) but-1-ene selectivity as a function of time (minutes). Reaction conditions: $P_{H_2} = 760$ Torr, $P_{HC} = 14.2$ Torr, $T_{reac.} = 273$ K or $P_{H_2} = 38$ Torr, $P_{HC} = 0.8$ Torr, $T_{reac.} = 263$ K.

totally converted into butane. At this point of the experiment if, conversely, we increased the hydrocarbon flow (F_1), the adsorption process was again operating and led to a 90% selective catalyst. Other flow decreases (F_2, F_4) led to another desorption peak. If, after that moment, the hydrocarbon flow was cut off, no desorption peak was observed in the fall of the katharometer signal. So, the desorption process observed there, on a stationary phase, was equivalent to the

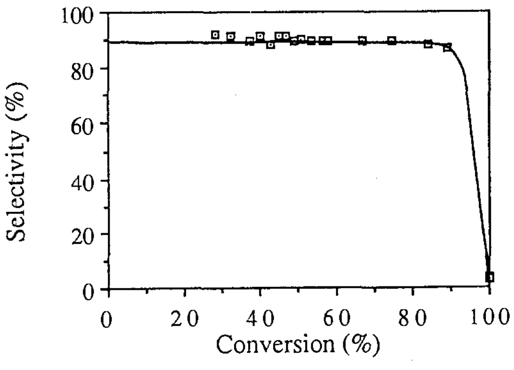

Fig. 3. But-1-ene selectivity (%) as a function of but-1-yne conversion (%). Reaction conditions are the same as in fig. 2.

one observed in fig. 1 during the final transient phase. We could see that *these adsorption-desorption processes were totally reversible.* In fig. 3, the but-1-ene selectivity obtained during the stationary phase was plotted as a function of the but-1-yne conversion. The selectivity remained 90% until 90% but-1-yne conversion was attained, afterwards it dropped rapidly.

4. Discussion

These results clearly show that, at the first contact times between the hydrocarbon and the catalyst, a hydrocarbon deposit made of strongly adsorbed but-1-yne molecules is formed. It plays a prominent role in the reaction. The increase in the selectivity comes from the fact that the hydrocarbon deposit takes over a lot of sites, impeding but-1-ene from readsorbing for further hydrogenation in butane. A simplified reaction scheme, as it was proposed before [4], can be written as follows:

$$\begin{tikzcd}
 & (\text{but-1-yne})_{g.} \arrow[d] & \\
(\text{but-1-yne})_{s.a.} \arrow[r, shift left, "K"] & (\text{but-1-yne})_{a.} \arrow[l, shift left] \arrow[r] & (\text{but-1-ene})_{g.} \\
A & B & C
\end{tikzcd}$$

(g. = gas, a. = adsorbed, s.a. = strongly adsorbed)

During the stationary phase, there is an equilibrium between A and B species and the transformation rate of B into C is constant. If the hydrocarbon flow is decreased, the quantity of but-1-yne in the gas phase decreases and, from a certain pressure limit, this leads to a drop in the quantity of B species. This loss of B species is compensated by an A to B equilibrium shift which makes A releasing adsorption sites available for hydrogen and but-1-ene and leads to a sharp rise in the transformation rate of B to C; therefore a desorption peak is observed which corresponds to the hydrogenation of every A species. The same phenomenon is observed during the transient final phase: after the hydrocarbon flow has been cut off at the entrance of the reactor, the but-1-yne gas pressure into the reactor becomes too low to maintain the adsorbed species equilibrium, so the A to B equilibrium shift leads to an increase of the B to C transformation rate and a desorption peak appears which is related with the total consumption of A species.

Up to now, we have not carried any further investigation to define the structure of A species. Nevertheless, we think that they cannot be considered as butylidyne because they behave quite differently from what was found by Beebe et al. [5] for ethylidyne species on palladium. These authors have shown, by in situ infrared spectroscopic investigation, that ethylidyne formation and hydrogenation occur during ethylene hydrogenation but with a rate 2 to 3 orders magnitude slower. In the present study, selective hydrogenation and A species formation and hydrogenation are not parallel reactions but A species are in equilibrium with the reactive species and their presence is a necessary condition for getting a selective catalyst. Moreover it is worth to underline that such an adsorbed species equilibrium is the key factor which governs the selectivity at high conversion (fig. 3): the selectivity drops when the equilibrium is broken. From an industrial point of view, it is interesting to retain the initial selectivity for a conversion as high as possible; that should be reached by using more appropriate experimental conditions since we have found that the number of hydrocarbon molecules which desorbed in the final transient phase varied in a large scale depending on the hydrogen and hydrocarbon pressures and the temperatures [6].

Acknowledgments

We thanks Dr. J.P. Boitiaux from the Institut Français du Pétrole, Rueil-Malmaison, for the gift of the sample. Thanks are also due to Dr. G. Maire for constant support.

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