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The role of carbonaceous deposits and support impurities in the selective hydrogenation of ethyne

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In order to elucidate the role of carbonaceous deposits, the hydrogenation of ethyne over silica supported Pt and Pd catalysts has been studied in a micro-pulse reactor. When a pure silica support (Aerosil) was used, the conversion decreased with an increasing number of ethyne pulses led over the reactor. Simultaneously, the selectivity towards ethene increased. When less pure silica (Kieselgel) was used as a support, the opposite effect was observed. These results are explained by assuming that the carbonaceous deposits are not active, but influence the selectivity of the uncovered metal surface by diminishing the average ensemble size available for the reaction. Impurities in the support can alter the behaviour of the catalysts.

Keywords: silica-supported catalyst; platinum; palladium; selective reduction of ethyne; hydrogenation; carbon layer; support impurities

1. Introduction

The hydrogenation of ethyne and acetylenic compounds is important to the chemical industry. Knowledge concerning these hydrogenation reactions can often also be applied to the hydrogenation of di-enes. Extensive reviews on this topic were published in the early sixties [1–3]. More recently, results have been reported on the effect of alloying and of particle size on the activity and selectivity in ethyne hydrogenation [4–10].

In 1976 an important, generalizing suggestion has been made concerning the mechanism of the reaction: the hydrogenation occurs on top of the carbonaceous deposits [11] that are formed at the start of the reaction. Ethyne adsorbed on the uncovered metal surface is too firmly bound to be active. Later, it was also established that a carbonaceous deposit – ethylidine – can exchange its hydrogen [12,13] and, therefore, Zaera and Somorjai suggested that the hydrogenation of ethyne occurred on this ethylidine [14,16]. Al-Ammar and Webb proved that an irreversi-

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bly bound carbon-rich layer was formed during the hydrogenation reaction, and they suggested, following ref. [11], that the reaction of hydrogen with ethyne takes place on top of these carbonaceous deposits [17–19].

These results, indicating that the hydrogenation proceeds on the carbon-rich layer, are at variance with the results presented in a short, but important communication by Hattori and Burwell [20]. They proved for the hydrogenation of cyclopropane that the presence of firmly bound species did not improve the catalytic activity of the metal catalyst, but suppressed it. However, no similar information is known with regard to ethyne hydrogenation, and it is possible that ethyne behaves differently from other unsaturated hydrocarbons. For example, palladium that is heavily loaded with lead is totally inactive in the hydrogenation of olefins, but it still can catalyse the reduction of ethyne. It is obvious that pulse experiments as performed by Hattori et al. [20] with ethyne can help in solving the problem.

During the course of the experiments, it appeared that impurities present in common commercial supports can play an important role in the hydrogenation of ethyne, in the same way as they do in syngas reactions [21]. So we also report on this problem.

2. Experimental

2.1. CATALYST PREPARATION

All catalysts were prepared by wet impregnation from a diluted HCl solution, the metal precursors used were $H_2Pt(OH)_6$ (Johnson Matthey) and $PdCl_2$ (Merck). The support used was SiO_2-Kieselgel (Merck, 480 m^2/g, 1200 ppm Na, 1000–1500 ppm Fe), SiO_2-Aerosil (Degussa, 200 m^2/g, 200 ppm Na, no Fe) [21], or SilicoAlumina (Akzo, 12% Al_2O_3, 400 m^2/g), the metal loading of the catalysts was 0.03 wt%. After 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 250°C for 3 h.

2.2. MICRO-PULSE APPARATUS

The experiments were performed at 297 K and at a pressure of approximately 1.6 bar. A hydrogen flow was continuously led over the reactor, and served simultaneously as the carrier gas of the gas chromatograph, which was directly connected to the reactor. Pulses of ethyne (200 µl) could be introduced into the hydrogen stream [22]. The gases used were checked for impurities by a mass spectrometer. No impurities above the detection limit (0.003%) were found.

The set-up allowed a direct analysis of each pulse and therefore offered an easy way to observe the effect of an increasing carbon deposition by simply comparing the results obtained with subsequent pulses. In a standard experiment, about 20 mg of catalyst was used.

The selectivity to ethene (S) and the conversion (α) are defined as follows:

$$S = \frac{P_{\text{ethene}}}{P_{\text{ethene}} + P_{\text{ethane}}} \times 100\%,$$

$$\alpha = \frac{P_{\text{ethene}} + P_{\text{ethane}}}{P_{\text{ethyne}} + P_{\text{ethene}} + P_{\text{ethane}}} \times 100\%.$$

P are the concentrations as determined (after calibration) by the gas chromatograph.

3. Results

It has been reported earlier that the catalytic bed can act as a chromatographic column [23]. In this paper it is argued that this phenomenon leads to splitting of the detected peaks, and that the splitting is dependent on the support material. This effect can also be seen in table 1. Both ethane and ethene show two separated peaks, which are designated here as I and II.

The first retention time of each product was independent of the conditions. The retention time of the second peak showed a dependence on both the support and the pulse number. Although the differences are not pronounced, they can be measured very well by the equipment used. When Pt/Kieselgel was used as a catalyst, no second peak of ethene could be detected. For the calculation of the selectivity and conversion both peaks of each product are taken together.

Figs. 1a and 1b show the results obtained with Pt and Pd catalysts supported on Kieselgel. Both catalysts show an increasing conversion and a decreasing selectivity at increasing pulse number. The reader will notice that Pd has a much lower selectivity than usually reported. Obviously, the results obtained with pulse experiments, during which the concentration of ethyne varies along the reactor, differ strongly from, for example, batch or steady-state flow experiments.

Table 1
Dependence of the retention time on the catalyst support and the duration of the reaction

Product	Pt/Kieselgel		Pt/SilicoAlumina	
	1th pulse	7nd pulse	1th pulse	7nd pulse
ethane I	2.7	2.7	2.7	2.7
ethane II	2.9	2.8	3.4	3.3
ethene I	3.9	3.9	3.9	3.9
ethene II	–	–	4.3	4.1

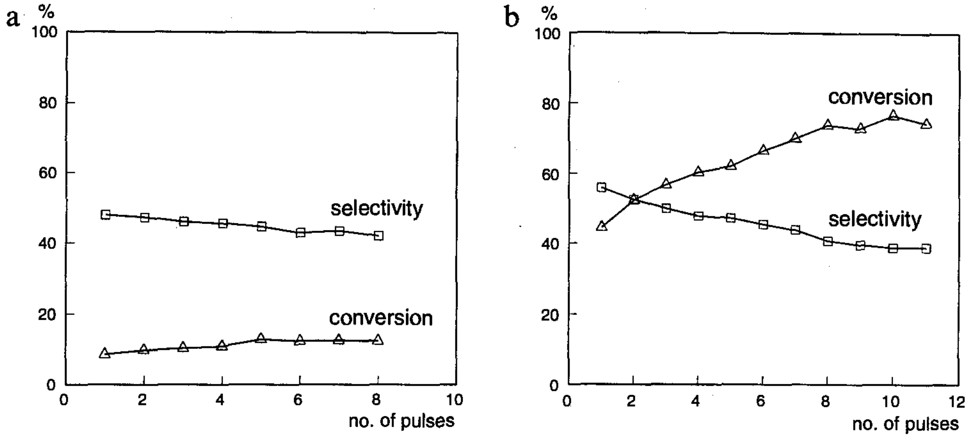

Fig. 1. Selectivity and conversion as a function of pulse number for (a) Pt/Kieselgel and (b) Pd/Kieselgel.

Surprisingly, the conversion increased with an increasing number of pulses. Such behaviour would be in compliance with the idea that the carbon-rich layer on the metal is the place where the hydrogenation occurs. However, it was at variance with low-pressure batch experiments we had performed: when Pt, Pd, and Ir were used in these experiments, the activity was lower in the repeated runs (with the same catalyst), but the selectivity was higher [22,24]. Thus, for the study described in this paper, platinum and palladium catalysts were prepared with Aerosil as a support.

The behaviour of Pt and Pd supported on Aerosil is shown in figs. 2a and 2b. There is a remarkable difference with fig. 1. In contrast to the Kieselgel supported

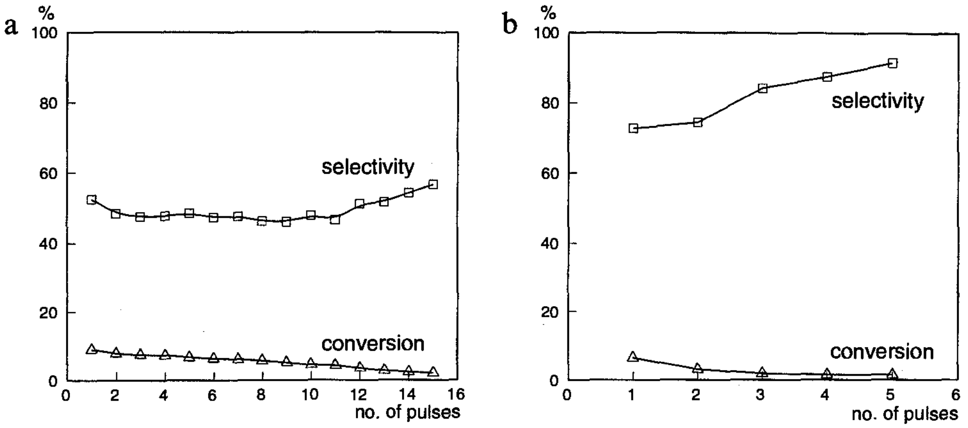

Fig. 2. Selectivity and conversion as a function of pulse number for (a) Pt/Aerosil and (b) Pd/Aerosil.

catalysts, the Aerosil supported catalysts show a decreasing conversion and an increasing selectivity with increasing pulse number.

A known difference between Kieselgel and Aerosil is the content of impurities (see the Experimental section). Impurities influence dramatically the reactions of syngas on rhodium and copper [21]. To clarify the role of support impurities in the reaction of ethyne, Kieselgel was leached with 12 M HCl before being used as a support. In another experiment, the HCl solution obtained by this leaching was used to impregnate pure Aerosil. The Aerosil treated in this way was then used as a support for a Pt catalyst. The results obtained with both catalysts are presented in figs. 3a and 3b.

The behaviour of the cleaned-Kieselgel supported catalyst is clearly different from the untreated-Kieselgel supported catalyst and it is more similar to that of Pt/Aerosil (fig. 2a). The behaviour of the Aerosil supported catalyst to which the impurities obtained from Kieselgel are added clearly resembles that of the Pt/(unpurified-) Kieselgel catalyst (fig. 1a). When 0.08 wt% of iron nitrate is added to the Aerosil supported catalyst, a similar trend is also observed.

4. Discussion

When clean silica (Aerosil) is used as a support, the conversion *decreases* with *increasing* pulse number. In batch experiments the activity also decreases when one catalyst is used repeatedly.

It is known that carbonaceous layers are formed on the metal surface during the hydrogenation of ethyne. As the conversion decreases with repeated reaction runs, while – at the same time – a carbonaceous layer is formed, it must be concluded that the carbon deposits are less active than the metal, or even completely

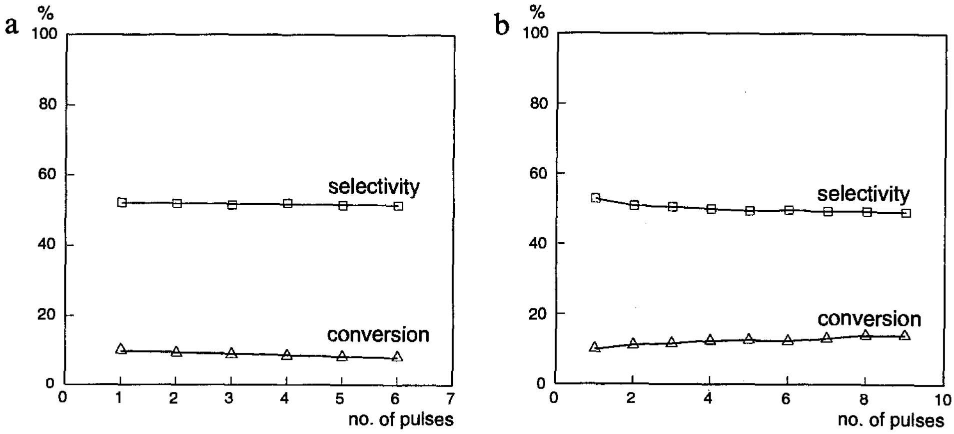

Fig. 3. Selectivity and conversion as a function of pulse number for (a) Pt/leached Kieselgel and (b) Pt/contaminated Aerosil.

inactive. As mentioned above, Hattori and Burwell came to the same conclusion in their study of cyclo-propane hydrogenation [20].

Al-Ammar and Webb claim, however, that during the steady state the carbon layer is the active part of the catalyst. Nevertheless, their own experiments showed a drop in activity during the initial stage of the reaction. This decrease is of the same size as the suppression of CO adsorption [17], which of course only takes place on the uncovered metal surface. Thus the clean metal surface could have been responsible for the surviving activity at the steady state, suggesting that the carbonaceous layer is inactive.

Al-Ammar and Webb also mentioned that, if the carbon layer provided the active sites, the selectivity would not be affected by the amount of carbon deposited [18]. As can be seen in fig. 2, an increasing pulse number – i.e., an increasing amount of carbon deposited – not only influences the activity, but also enhances the selectivity. This effect is exactly the same as found when iridium, which is an active metal, is alloyed with a less active element (copper) or with an inactive one (gold) [5]. In all three cases the selectivity increases.

As it is known that reactions involving acetylenic compounds can be structure sensitive [8,9] we might formulate a self-consistent explanation of these results. The ideas based on the ensemble-size effect [4] can, namely, explain several findings satisfactorily. Large ensembles are able to form multiple metal–carbon bonds, and, therefore, are probably sites for the formation of ethane via strongly bound intermediates. By carbon deposition or by alloying with an inactive metal, the average available ensemble size of the active metal is diminished. Thus the formation of ethane is suppressed, resulting in a higher selectivity to ethene [5,7,10]. This picture is also consistent with results reported by Teratani and Hirota, who used nickel catalysts [25]. Very recently, Jackson et al. showed – for propyne hydrogenation – that deactivation of a Pt/silica catalyst occurred when carbon was deposited and that this had a positive effect on the selectivity [26].

Impurities in the support influence dramatically the performance of a catalyst. The selectivity of platinum on a clean support, such as Aerosil, rises when the number of pulses increases (fig. 2a). If the Aerosil support is deliberately polluted with contaminations extracted from Kieselgel or with iron nitrate, the Pt catalyst shows a decreasing selectivity with increasing pulse number. This decrease of selectivity is also seen on Kieselgel-supported catalysts. Therefore, contaminants in the support – e.g., iron – probably cause the difference in performance between the Kieselgel- and Aerosil-supported catalysts.

Two different explanations for the effect of support contamination can be proposed. First, it is possible that the impurities stabilize metal ions, which have different catalytic properties compared with zero-valent metal. During the reaction the oxidation state can be changed by the reactants, and thus increase the active surface of the catalyst. A second, more attractive, explanation is that impurities are leached out of the support either during the preparation of the catalyst or during the reaction, and are subsequently deposited on the catalyst surface. There they could promote the activity of the catalyst, at cost of a high selectivity. A promotion effect of support impurities is described earlier for syngas reactions [21].

The existence of two peaks for each product can be explained by the capability of impurities in the support to adsorb – and thus retain – hydrocarbons. Ethyne stored in this way can react in a later stage by the so-called reverse spill-over towards the metal. The same mechanism has, for example, been suggested for CO oxidation on supported Pd [27]. This also explains the increase in retention time of the second peak when a more strongly binding (acidic) support is used (table 1). The decrease in retention time during the experiment could then be caused by poisoning of the adsorption sites on the support.

5. Conclusions

Carbonaceous deposits are not active in the hydrogenation of ethyne. However, they change the direction of the reaction in such a way that ethene formation is favoured. This is probably caused by the fact that on surfaces with carbonaceous deposits the uncovered metal sites consist of smaller ensembles. Smaller ensembles bind less strongly ethyne and, therefore, produce the less hydrogenated ethene instead of ethane.

Impurities in the silica support can alter the behaviour of the catalyst.

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