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NOTE

Incorporation of Deuterium in Coke Formed on an Acetylene Hydrogenation Catalyst

In selective hydrogenation of acetylene in excess ethylene, considerable amounts of coke or "green oils" are formed and accumulate on the catalyst. A fraction of the acetylene undergoes oligomerization reactions producing C_4's and larger hydrocarbons. Compounds larger than C_8 are retained on the catalyst surface or as a condensed phase in the pore system. The reaction mechanism is largely unknown but several authors have postulated that oligomerization occurs through dissociatively adsorbed acetylene (1, 2), i.e., C_2H(ads) and C_2(ads). Battiston *et al.* (3) and Yayun *et al.* (4) have found that the rate of coke deposition increases with increasing acetylene pressure, while the role of hydrogen appears more complicated. Battiston *et al.* (3) have shown that no coke formation occurs if no hydrogen is present in the gas. On the other hand, for a hydrogen-to-acetylene ratio in the interval 1.5–4, increasing the hydrogen pressure suppresses coke accumulation (4). Most authors agree that ethylene is not involved in the oligomerization. McGown *et al.* (5) has presented perhaps the most elegant proof of this conclusion; they replaced ethylene by propylene and found no detectable C_5 formation.

In this paper a novel method of studying the coke formation on a catalyst is introduced. Deuterium is incorporated in the coke during hydrogenation of acetylene, and during temperature-programmed oxidation (TPO) experiments the deuterium content is analyzed. The objective is to shed some light on the mechanism for oligomer formation in this system.

The catalyst, Pd/α-Al_2O_3, was prepared by the impregnation of α-alumina (Süd-Chemie) with a solution of $Pd(NO_3)_2$ in 30% HNO_3. Impregnation was followed by drying at room temperature for 24 h and at 393 K for 16 h. Calcination in air at 723 K (3 h) and reduction in a 1:9 mixture of hydrogen and nitrogen at the same temperature concluded the preparation. Before each experiment the catalyst was rereduced at 523 K for 3 h in 10% hydrogen or deuterium and cooled to the reaction temperature in flowing nitrogen. Characterization results are given in Table 1.

The experiments were carried out in an internal recycle (Berty) reactor. Acetylene conversion and reactant concentrations were kept constant during a whole run of 24 h (further details are given elsewhere (6)). The reaction conditions were: temperature, 313 K; total pressure, 1 MPa; acetylene pressure, 6.8 kPa; ethylene pressure, 0.3 MPa; and hydrogen or deuterium pressure, 7.3 kPa. When hydrogen was replaced by deuterium during the reaction, the latter was used also for catalyst reduction. Hence, there was no adsorbed or absorbed hydrogen present on the catalyst in the deuterium run.

Temperature-programmed oxidation (TPO) was used to study coke formed on the catalyst. About 100 mg of deactivated catalyst was placed in a flow reactor, Fig. 1. Oxygen (1 ml/min) and nitrogen (24 ml/min) were flushed through the catalyst bed and the temperature was increased from 300 to 953 K at a heating rate of 10 K/min. After the main oven, a second oven heated a part of the reactor containing a platinum foil. The temperature was kept at 673 K through the whole experiment and desorbing species were oxidized by the platinum. The advantage with this setup is that it is possible to quantify all coke on the catalyst, even coke that desorbs from the catalyst at relatively low temperature.

The TPO experiments were performed using a mass spectrometer (MS), Gaslab 300, Fisons Instruments. The mass numbers that were identified were *M/e* 44 (CO_2), *M/e* 32 (O_2), *M/e* 18 (H_2O), *M/e* 19 (HDO), and *M/e* 20 (D_2O). By burning different concentrations of acetylene, the CO_2, H_2O, and O_2 responses were calibrated. Mixtures of H_2 and D_2 were oxidized to determine the responses of H_2O, HDO, and D_2O. The hydrogen-to-carbon ratio in the coke was estimated from the CO_2 and H_2O formation.

Catalysts coked without deuterium were treated with deuterium at 313 and 673 K respectively for 3 h. A fresh catalyst was also treated with deuterium at 313 K. The experiments were conducted in order to see if incorporation of deuterium into the coke or on the support could take place after the reaction was stopped.

The reaction rate for the acetylene hydrogenation decreased by 9% when hydrogen was replaced with

TABLE 1

Pd load (wt%)	Dispersion (mole CO/mole Pd)	Pore volume (cm^3/g)	BET surface (m^2/g)
0.05	0.035	0.23	8

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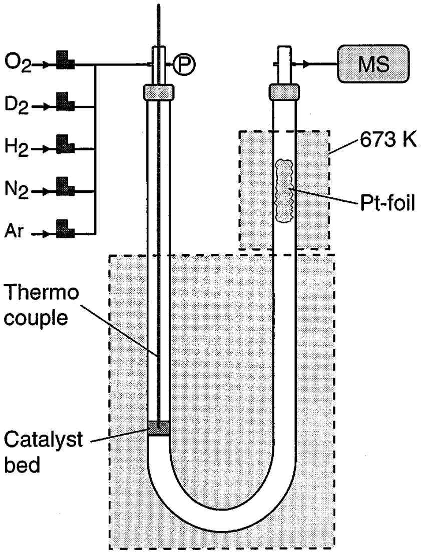

FIG. 1. The experimental setup for the TPO experiments.

deuterium. This is in agreement with previous work (7). The amount of coke decreased by 6% due to the change of isotope.

The TPO profile from the experiment where acetylene was hydrogenated using hydrogen is shown in Fig. 2, which also shows the hydrogen-to-carbon ratio. The ratio is about 1.5 for the main peaks around 600 K. The amount of deuterium has been evaluated from *M/e* 18, *M/e* 19, and *M/e* 20. The H/D ratio for the coke obtained during the experiment where deuterium was used for the acetylene hydrogenation is shown in Fig. 3. It is found to be slightly larger than 2 over the whole temperature range.

In order to account for effects of deuterium exchange with hydrogen in the coke or on the surface, experiments were performed where catalysts coked without deuterium, but otherwise equal reaction conditions, were exposed to deuterium at 313 and 673 K followed by TPO. At the high temperature most of the coke is removed before the TPO experiment. The amount of deuterium determined from *M/e* 19 can be found in Fig. 4.

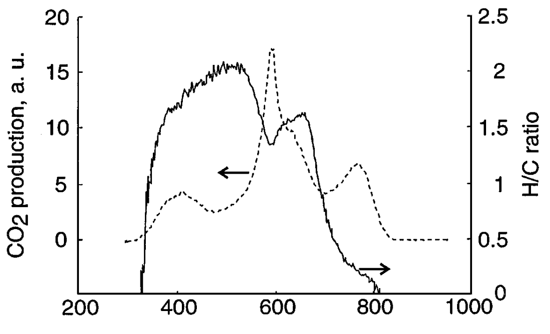

FIG. 2. The TPO profile and the H/C ratio for the catalyst deactivated during hydrogenation with hydrogen.

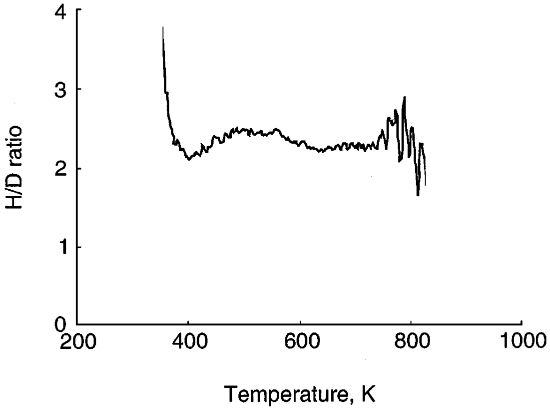

FIG. 3. The H/D ratio in coke obtained during hydrogenation of acetylene with deuterium.

In Fig. 4 it is observed that relatively little deuterium is exchanged on the catalyst during the treatment at 313 K. The catalyst that has been treated at 673 K shows higher deuterium exchange. The fresh catalyst that was treated with deuterium at 313 K did not release any traces of HDO. This indicates that deuterium is not exchanged in any detectable amounts on the carrier. No traces of deuterium were found on a catalyst deactivated without deuterium and not treated with deuterium afterward.

The method of using deuterium during the deactivation and analyzing the coke according to the deuterium content during TPO has proven to work. When applying the method it is important to determine if any deuterium may be exchanged with hydrogen on the coke already formed during the coking reaction. We have seen that this is not the case at our reaction temperature (313 K).

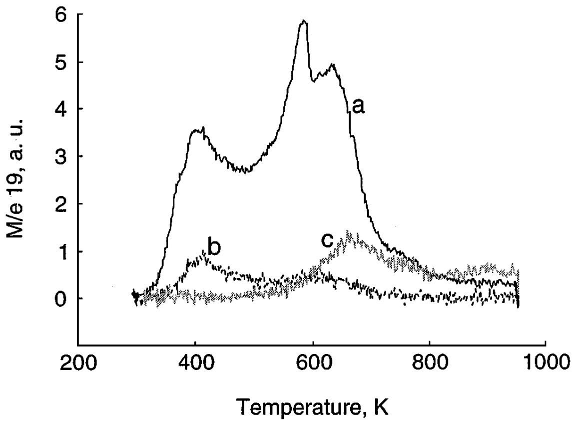

FIG. 4. *M/e* for (a) the catalyst deactivated using deuterium; (b) the catalyst deactivated without deuterium but treated with deuterium at 313 K for 3 h; and (c) the catalyst deactivated without deuterium but treated with deuterium at 673 K for 3 h.

The average coke composition obtained from the TPO results gives approximately the following overall stoichiometry for the coking reaction(s):

$$nC_2H_2 + \frac{n}{2}D_2 \rightarrow nC_2H_2D(\text{ads})$$

These results show that hydrogen (or deuterium) from the gas phase is a reactant in oligomerization, as a considerable amount of deuterium is incorporated in the deposited coke. Further, our observations cast some doubt on the idea that oligomers and coke originate from dissociatively adsorbed acetylene. If this had been the mechanism, we would have expected a much higher deuterium content (a lower H/D ratio).

We can still only speculate about the reaction mechanism, but a plausible route is that oligomerization occurs through reactions involving a half-hydrogenated intermediate with the composition C_2H_3 or C_2H_2D. Such a species occurs in the previously proposed mechanisms for acetylene hydrogenation to give ethylene (1, 2). If the coverage of adsorbed hydrogen atoms is low, the half-hydrogenated species may react with other surface species, leading to dimers or larger chains. This mechanism also explains the complicated influence of the hydrogen pressure: if the hydrogen surface coverage is very low, the half-hydrogenated intermediate is diminished and no hydrogenation or oligomerization occurs. At high coverage of hydrogen, the probability for hydrogenation to ethylene increases and the intermediates are consumed before oligomerization can take place.

Dimerization of C_2H_3(ads) is expected to give 1,3-butadiene, a compound which is readily formed during acetylene hydrogenation, particularly at high acetylene pressures (5). This may be an important intermediate in oligomerization, as conjugated dienes polymerize rapidly in the presence of a catalyst with an acid-like function. According to Boitiaux *et al.* (8), oligomer formation is governed by the soft acidity of palladium. A noteworthy result in this context is the observation by Asplund (6) that coke deposition can take place on pure γ-Al_2O_3, but only if a Pd catalyst is also present in the reactor. This implies that the weakly acidic surface of γ-Al_2O_3 can catalyze oligomerization of some precursor formed on the Pd surface and transferred to the alumina via the gas phase. Butadiene seems a likely precursor candidate, being volatile, easily polymerized, and formed in appreciable amounts in acetylene hydrogenation.

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