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THE ROLE OF THE CARBONACEOUS OVERLAYER IN THE COMPETITIVE HYDROGENATION OF CYCLOPROPANES AND OLEFINS

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In the competitive hydrogenation of olefin-cyclopropane mixtures (2-Me-2-butene + 1,1-diMe-cyclopropane and 2,4-diMe-2-pentene + 1,1,2,2-tetraMe-cyclopropane) over silica supported Pt, Pd and Rh catalysts at 318 K and 373 K, only the olefin is hydrogenated. The other component does not react even after the complete hydrogenation of the olefin. The olefin creates a hydrogen-rich carbonaceous overlayer which is the active phase for its hydrogenation but it is a permanent poison for the hydrogenative ring opening of the cyclopropane ring. On Ni/SiO_2 at 473 K, however, such an overlayer does not form and both reactants transform in parallel in a complex way.

In his early paper [1], Maxted mentioned the toxic effect of compounds containing multiple bonds on the various transformations of more saturated materials over metal catalysts. Without citing original papers, he claimed that this effect was due to a mere competition: the more strongly held substrate prevented the adsorption of the other. It follows that the more strongly adsorbed compound acts like an apparent poison until its reaction is over, and after this the other component starts to react.

We have recently studied the ring opening reactions of differently substituted cyclopropanes over supported metal catalysts in hydrogen atmosphere in a static circulation system. In some experiments we attempted competitive reactions with a substituted cyclopropane and an isomeric olefin. The reactant pairs were either 1,1-diMe-cyclopropane + 2-Me-2-butene or 1,1,2,2-tetraMe-cyclopropane + 2,4-diMe-2-pentene. The olefins were products of Aldrich Chemical Co., while the cyclopropanes were prepared and purified according to the literature [2,3]. The olefins were gas chromatographically pure and were subjected to several freeze-evacuate-thaw cycles before the reaction. Further, the olefin with higher molecular weight (the 2,4-diMe-2-pentene) was passed through a column filled with freshly activated basic alumina (Camag) under inert (N_2) atmosphere before preparing the reaction mixture. The catalysts were low-dispersion silica-supported (Cab-O-Sil M5, BDH product) Pt, Pd, Rh and Ni. The circulation system and the catalysts have been described elsewhere [4,5]. The reaction was monitored by GC. The reaction conditions and the dispersion data can be found in table 1.

For the Pt, Pd and Rh catalysts (5 mg was used), we ran the reactions at 318 K or at 373 K: only the olefin was hydrogenated and the hydrogenation was

Table 1
Reaction conditions for the competitive hydrogenation of 1,1-diMe-cyclopropane + 2-Me-2-butene mixtures

Catalyst	Dispersion (%)	Olefin content (mole%)	Hydrogen pressure (kPa)	Temperature (K)
3.0% Pt/Cbs	15.9			
fresh		10.9	26.7	318
used		11.0	20.0	318
fresh		4.8	33.3	373
3.0% Pd/Cbs	15.4			
fresh		4.5	10.0	318
used		4.5	10.0	318
used		10.9	39.9	373
3.2% Rh/Cbs	27.0			
fresh		4.5	39.3	373
used		10.9	26.0	318
3.0% Ni/Cbs	6.8			
fresh		15.0	8.3	473
fresh		15.0	26.8	473

Notes: 1. Cbs = Cab-O-Syl M5.
2. The dispersion data were determined by hydrogen chemisorption.

complete by the time the first sampling occurred (5 min). There was no cyclopropane hydrogenation whatsoever even after 100 min. The used catalysts were capable of hydrogenating the olefin from new olefin + cyclopropane mixtures several times (with total conversion before the first sampling) without any impact on the other component. The important feature of this reaction is that the olefin, even after its complete hydrogenation, acts as a permanent poison for the transformations of the cyclopropane, irrespective of the hydrogen pressure. Nevertheless, after the hydrogenation of the olefin in the mixture, a fresh sample of catalyst (5 mg) will hydrogenate the cyclopropane. The saturated hydrocarbons, resulting from the previous hydrogenation of the olefin and from the ring opening of the cyclopropane do not influence the kinetics of the ring opening reaction. That is, the rate of the hydrogenative ring opening of the pure (olefin free) cyclopropane was the same (within ±5%) as that of the cyclopropane after previously hydrogenating the olefin. Doubling the quantity of the catalyst (from 5 mg to 10 mg) did not change the phenomenon.

It is interesting that the behavior of Ni/Cab-O-Sil was different under similar conditions but at 473 K. This catalyst was not poisoned by the olefin residues, but both the olefin and the cyclopropane were hydrogenated and the isomerization of the cyclopropane occurred as well.

Thus, we may say that the olefin hydrogenation proceeds on a different surface than the ring opening, and the mechanism of the transformations on Pt, Pd and

Rh differs from that on Ni (perhaps because of the very different temperature applied).

In the original mechanistic consideration for the hydrogenation of olefins, Horiuti and Polanyi presumed that the * R * and RH * species are formed on the surface metal atoms [6]. Later, Hansen et al. pointed out that the hydrogenation might proceed on a layer of adsorbed olefin and that the reaction occurs via a hydrogen transfer mechanism [7,8]. The hydrogen-rich adsorbed species serve as a hydrogen pool for the molecules adsorbing in the second layer. From their results concerning the separate and competitive hydrogenation of ethylene and acetylene at 298 K over supported Pd, Rh and Ir catalysts, Webb et al. [9–12] concluded that the adsorption of these molecules occurred irreversibly in two separate stages: a non-linear primary region, in which the hydrocarbon species are predominantly dissociatively adsorbed, and a linear secondary region. Hydrogenation catalysis is associated with the hydrocarbon species adsorbed in the secondary region. From ^{14}CO studies in a static system, it was concluded that the hydrocarbon primary region was associated with the metal, whilst the secondary region probably involved the formation of overlayers on the primarily adsorbed species.

The role and nature of carbonaceous overlayers and the mechanism of coking have been studied extensively by Somorjai and his co-workers on single crystals [13,14]. In several cases their results can be directly applied to catalytic conditions, because they developed the technique to combine the tools of surface science with real life catalysis using a low-pressure high-pressure apparatus which can be used either in batch or in flow mode [15]. They determined the lifetime and the structure of these layers, and the effects of temperature on their formation and transformations. It was shown that not all kinds of carbonaceous deposits caused deactivation. Hydrogen-rich hydrocarbon species can play a decisive role, e.g. in hydrogenation reactions taking part in the catalytic action by transferring hydrogen to the second layer to be hydrogenated. For instance, cyclohexane is actually hydrogenated on an active carbonaceous overlayer like this, between 298 and 373 K, which is why this reaction is structure insensitive on Pt single crystals with different surface structures in this temperature range [16], in complete accordance with the results of Boudart et al. on supported Pt catalysts [17,18]. On Pt(111) and Rh(111) surfaces, in the hydrogenation of ethylene, propylene and butene, the active overlayer is non-linear and is formed by ethylidyne, propylidyne or butylidyne surface species, respectively [19]. It was found [20] that the properties of the alkylidyne layer depended strongly on the temperature. There is no alkylidyne layer below 300 K and it decomposes at about 400 K, so its importance is restricted largely to hydrogenation reactions which may occur in this temperature range. This layer is not the reaction intermediate, neither does it belong to the reaction pathway, but serves only to provide H atoms for the addition to the molecules adsorbed on top of these species. As the temperature increases, more and more dehydrogenated, and finally a graphitized layer forms.

It is worthwhile to mention, however, that the structure of adsorbed ethylene over different Pt surfaces (single crystals, supported and unsupported Pt catalysts) is still extensively debated. As we have seen above, it is ethylidyne over Pt(111) [19]. Infrared spectroscopy shows a variety of species over supported catalysts: σ-diadsorbed species with differing C-C bond orders and number of hydrogen (21), π-complexed form [22,23] together with δ-diadsorbed species [22], ethylidyne [24]. Solid state NMR studies also show contradictory results: e.g. Wang et al. [25] found ethylidyne while Gay [26] proposed π-bonded intermediate. The determination of the exact structure is important and may provide with further information about the formation and properties of the overlayer.

The high temperature sensitivity of the hydrogen-rich carbonaceous overlayers explains why Hattori and Burwell [27] could find no evidence of a hydrogen transfer mechanism through adsorbed hydrocarbon species in the hydrogenation of ethylene at 247 K.

On the other hand, Burwell and Butt and Somorjai all agree that the ring opening reactions of cyclopropanes [28] and of Me-cyclopentane [29] occur on bare metal atoms: the C-C bond breaks on the kink sites of the single crystal.

Thus, in the hydrogenation of the reactant pairs, 1,1-diMe-cyclopropane + 2-Me-2-pentene and 1,1,2,2-tetraMe-cyclopropane + 2,4-diMe-2-pentene, we may conclude that over silica supported Pt, Pd and Rh catalyst:

- the olefins are hydrogenated on an active carbonaceous overlayer at 318 K and at 373 K (and very probably in this temperature range);
- the cyclopropanes do not react on this surface, but on bare metal atoms;
- in the competitive hydrogenation, the olefin acts as a permanent poison;
- the hydrogen does not remove the overlayer in the course of the reaction;
- the used catalyst can hydrogenate the olefin from new mixtures several times, without apparent loss of activity.

More sophisticated instrumentation (e.g. microbalance-GC-MS) would make possible accurate mass balance measurements which should reveal more details about the properties of these overlayers.

On the Ni/SiO_2 catalyst, however, the above phenomena were not observed. The reactions (olefin hydrogenation and cyclopropane ring opening) proceeded in parallel, which shows that, as the temperature increases the role of the carbonaceous deposit changes: it is no longer an active overlayer, but a permanent poison which gradually deactivates the catalyst, and no longer allows fine distinctions between the mechanisms of the two reactions. For instance, the cyclopropane ring also opens through isomerization.

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