Continuous semihydrogenation of a propargylic alcohol over amorphous $Pd_{81}Si_{19}$ in dense carbon dioxide: effect of modifiers

Reto Tschan [a], Markus M. Schubert [a], Alfons Baiker [a,*], Werner Bonrath [b] and Hans Lansink-Rotgerink [c]

[a] Laboratory of Technical Chemistry, Swiss Federal Institute of Technology, ETH Zentrum, CH-8092 Zurich, Switzerland
E-mail: baiker@tech.chem.ethz.ch
[b] Vitamins and Fine Chemicals Division, Chemical Process Technology, F. Hoffmann-La Roche Ltd., CH-4070 Basel, Switzerland
[c] Degussa AG, Rodenbacher Chaussee 4, 63403 Hanau, Germany

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The influence of chemical modifiers on the semihydrogenation of a propargylic alcohol, dehydroisophytol, was studied in a continuous-flow reactor over amorphous $Pd_{81}Si_{19}$, employing dense carbon dioxide as solvent. All organic modifiers were able to improve the selectivity, however, at the expense of a lowered conversion. The extent of the effect depended strongly on the number of heteroatoms and on the specific structure of the modifier applied. For maximum isophytol yield, a compromise between high selectivity and reasonable conversion proved to be beneficial, with propyl disulfide and isopropyl disulfide representing the best choices under the applied conditions. Apart from choosing the appropriate modifier, selectivity could also be tuned by adjusting the modifier concentration. Our observations are consistent with a model including competitive adsorption of reactants and the modifier. Different effects of structural isomers imply that, at least partly, steric effects are involved. Compared to the organic modifiers, the use of a lead-modified catalyst could hardly improve the selectivity at a given conversion under the applied conditions.

KEY WORDS: selective hydrogenation; supercritical carbon dioxide; semihydrogenation of triple bonds; chemical modifiers; metallic glasses; alkinol; Lindlar reduction

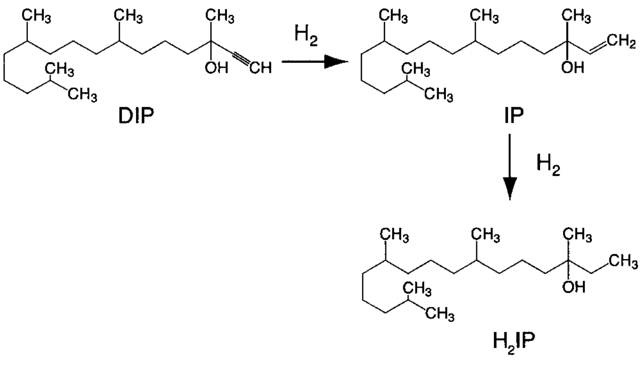
1. Introduction

Palladium is well known to catalyze the semihydrogenation of alkynes to alkenes (Lindlar reduction). Modifiers are often employed to increase the alkene selectivity. Historically, Lindlar suggested a $Pd/CaCO_3$ catalyst, poisoned by lead acetate, and quinoline as an additional modifier [1]. Alternatively, in later studies other organic bases, such as pyridine or ammonia, organic sulfides or CO were suggested as possible modifiers for the partial hydrogenation of various alkynes [2–5].

Model reaction in this work is the continuous semihydrogenation of the C–C triple bond in dehydroisophytol (DIP), a propargylic alcohol, to the corresponding alkenol, isophytol (IP) (scheme 1), employing an amorphous $Pd_{81}Si_{19}$ catalyst and dense ("supercritical") carbon dioxide as solvent. This reaction represents a prominent step in the industrial synthesis of Vitamin E [6]. High space-time yields at reasonable selectivities (*i.e.*, avoiding overhydrogenation of IP to dehydroisophytol, H_2IP; scheme 1) are required for the design of an efficient and economic process.

Previous studies showed that amorphous metal alloys ("metallic glasses"), such as $Pd_{81}Si_{19}$, are particularly suited for such semihydrogenation reactions, when compared, *e.g.*, to conventional supported catalysts [7]. Detailed information on the preparation and the specific advantages of metallic glasses in heterogeneous catalysis can be found in the pertinent literature, *e.g.*, [8,9].

Dense ("supercritical") CO_2 was employed as solvent, since supercritical fluids generally combine numerous advantages, such as process intensification, a favorable combination of heat and mass transfer, and a facile separation of solvent and product/reactants [10,11]. Moreover, carbon dioxide is non-flammable, environmentally benign, and readily available at low cost, when compared to most other standard solvents [12,13]. Note that the term "supercritical" is used here between quotation marks for the CO_2-containing dense phase at temperatures exceeding its mixture critical point (irrespective of further liquid phases present). In fluid theory, however, the expression is well defined only for single component systems and has no mean-



Scheme 1. Hydrogenation of dehydroisophytol (DIP) to isophytol (IP) and the consecutive hydrogenation of IP to dihydroisophytol (H_2IP).

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* To whom correspondence should be addressed.

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ing concerning the phase behavior of multicomponent systems [14].

In a parallel study [15], we investigated the phase behavior of the reaction mixture and the resulting implications on the catalytic behavior of $Pd_{81}Si_{19}$ during continuous semihydrogenation of DIP in a flow reactor using dense CO_2 as solvent. These studies indicated that under the reaction conditions used, the reaction mixture consists of two phases, a DIP-rich liquid phase and a dense CO_2-rich phase, both mutually saturated under equilibrium conditions.

Here we explored the effect of chemical modifiers on the selectivity and conversion under such uncommon conditions. Various organic modifiers, as well as lead modification (as a representative for an inorganic modifier) of the catalyst, were employed. It will be shown that all organic modifiers had a significant impact on the selectivity; the effect, however, strongly depended on the heteroatom(s) included in the structure of each specific modifier. Subsequently, the concerted action of a pair of suitable modifiers will be focused. This will demonstrate that a precise tuning of the selectivity/activity can be achieved by choosing the appropriate modifiers and concentrations. Finally, comparison with a lead-poisoned catalyst reveals that this frequently used inorganic modifier is rather ineffective under the applied reaction conditions.

2. Experimental

Measurements were conducted in a computer-controlled continuous-flow reactor of mini plant scale. The reactor system comprised a mixing chamber, a vertically mounted reactor section (down stream concept) and a sampling device at the reactor outlet. The experimental setup has been described in detail elsewhere [15].

All feed streams (CO_2, H_2, and DIP) were combined in a mixing chamber before entering the reactor section. The inner diameter of the reactor tube (stainless steel, closed by steel frits towards both ends) was 10 mm. The catalyst needles were fixed by quartz wool plugs, resulting in a catalyst bed length of *ca.* 30–100 mm depending on the amount of $Pd_{81}Si_{19}$ used. Temperature was controlled separately for the mixing chamber and the reactor section using two independent thermostats. Constant pressure was maintained by a backpressure regulator. DIP was pumped into the reactor system by a HPLC pump. Organic modifiers were dissolved in the DIP before feeding to the reactor.

All experiments were performed over a $Pd_{81}Si_{19}$ amorphous metal alloy (metallic glass), prepared by Degussa-Huels AG. The $Pd_{81}Si_{19}$ needles, of *ca.* 0.13 mm diameter, had a surface area of approximately 0.01 $m^2\,g^{-1}$, as was determined using the BET method with krypton.

The Pb-poisoned sample was prepared by stirring 3 g of $Pd_{81}Si_{19}$ flakes in an aqueous solution (*ca.* 100 ml) of 50 mg lead acetate with traces of conc. acetic acid for 45 min at 80 °C. After filtering, the flakes were dried at 80 °C in 100 mbar N_2. Subsequent XPS measurements [16] revealed a composition of 71% O, 14.7% Si, 13.7% Pd, and 0.6% Pb, which would correspond to a Pd/Pb ratio of roughly 10 : 1 on the surface. In as-prepared catalyst lead was present in

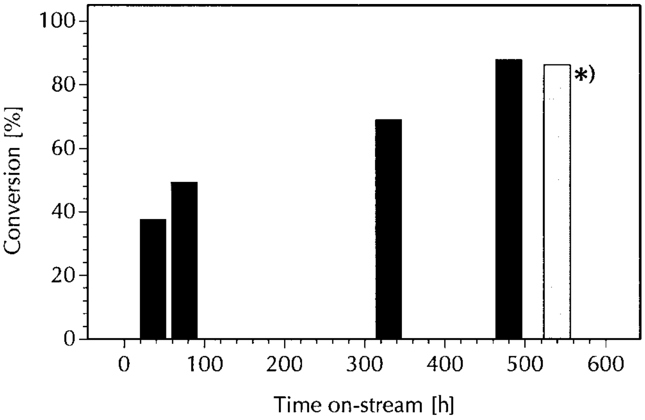


Figure 1. Increase of activity of the catalyst with time on-stream. Repetitive experiments under identical reaction conditions: $T = 86\,°C$, $p = 127$ bar, 2,2′-(ethylendithio)-diethanol added to the DIP feed (1 : 2000 mol mol^{-1}), $m_{catalyst} = 9$ g (*: 3 g).

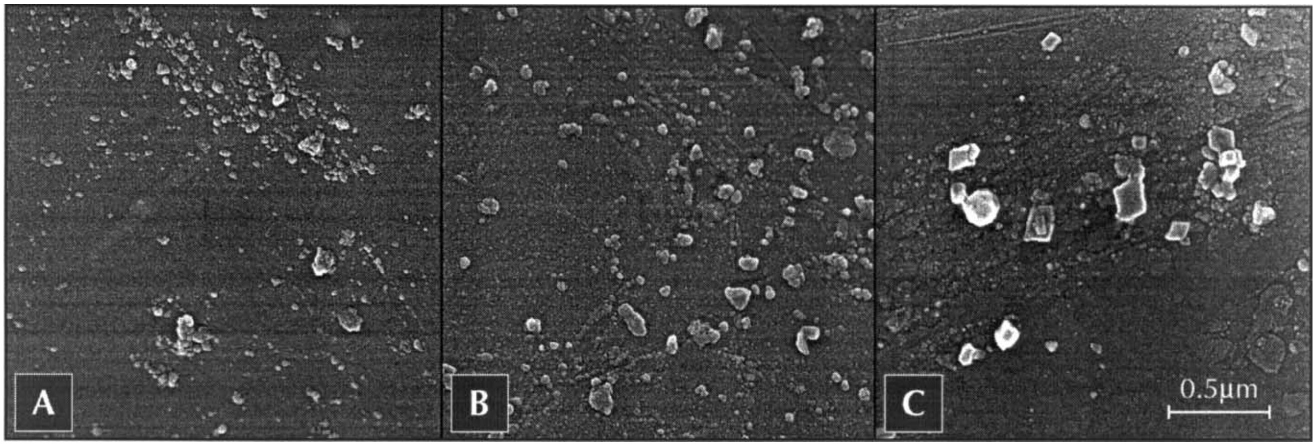


Figure 2. Scanning electron micrographs of the catalyst surface: (A) as received, (B) after 6 h on-stream (DIP without modifier), and (C) at the end of the experimental series of this study. Images were acquired on a Hitachi S-900 “in-lens” field emission scanning electron microscope operated at 30 kV.

metallic and ionic form. During reaction, however, lead was reduced to zero-valent Pb.

Reaction conditions were: $T = 86\,°C$, $p = 127$ bar, CO_2 flow $= 160$ Nl h^{-1}, H_2 flow $= 20$ Nl h^{-1}, and DIP flow $=$ 38 g h^{-1}, corresponding to a molar ratio of $CO_2 : DIP : H_2$ of 56 : 1 : 7. The typical w/F ratio (weight of catalyst to DIP flow) was 25–70 g s mol^{-1}.

Sampling occurred automatically. Samples were analyzed by a GC (HP 6890, equipped with a J&W FS DB-5-HT column and flame-ionization detector). A small amount of by-product formation ($<1\%$) was observed, consisting of compounds with high boiling points, which will be referred to as oligomers in this work. Concentrations of DIP, IP, H_2IP, and oligomers were determined on basis of GC area%, which were previously calibrated by samples of known composition. Selectivity is defined as $[IP]/([IP] + [H_2IP] + [oligomers])$. Steady-state was reached after *ca.* 3–4 h; therefore, all presented values were recorded after 4–6 h on-stream.

It should be mentioned that the catalyst activity was observed to slowly increase (irreversible) for repetition experiments conducted under identical conditions in the course of our study (figure 1). XPS and SEM images revealed drastic changes in composition and morphology of the catalyst surface. The fresh catalyst featured some small scattered particles (assumingly pure Pd) attached to an otherwise smooth surface (figure 2(A)). After just one experimental run (6 h), first alterations of the surface structure became apparent, *i.e.*, agglomerating of the particles and roughening of the underground (figure 2(B)). Finally, at the end of all experimental series, the surface had become very rough and larger crystallites were seen on top (figure 2(C)). Concomitantly, XPS indicated a strong enrichment in Pd within the surface layer. Furthermore, a black deposit was clearly visible on the Teflon insert in the mixing chamber and the mixer after a long experimental series. Molnar *et al.* observed the same phenomenon when hydrogenating terminal alkynes over Pd catalysts [7]. It was suspected that part of the metal dissolved by complexation with the terminal alkyne. They found that some catalysts, which had been inactive for the hydrogenation of olefins, could be activated by first running the hydrogenation of a terminal alkyne. Efforts to detect an R–C≡C–Pd compound in the solution by IR, however, failed [7]. Likewise, our own AAS analysis could not detect any palladium in the product stream (detection limit 4 ppm).

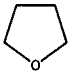
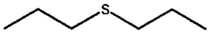
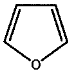
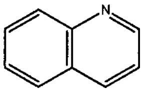
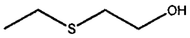
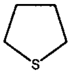
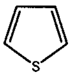
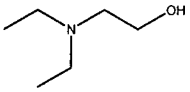
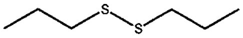
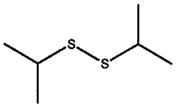
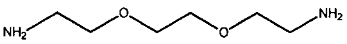
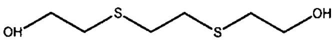
To cope with this problem the data of each experimental series was recorded at intervals as short as possible in order to keep deviations small. Although, measurement series at the very beginning and at the end of this study may differ in the absolute conversion values, due to the above effect, the relative outcome within each series was hardly affected. Therefore, our general conclusions are independent of such long-term changes in catalytic activity (for further details see [16]).

3. Results

3.1. Organic modifiers

For the semihydrogenation of DIP under such uncommon conditions, a recent patent assigned to Hoffmann-La Roche AG suggested 2,2′-(ethylendithio)-diethanol as a suitable modifier in order to increase the selectivity to IP significantly [17]. Table 1 provides an overview on the modifiers

Table 1
Overview of employed modifiers along with observed conversion, selectivity, and IP yield, respectively. All modifiers were added to the reactant (DIP) in a mole fraction of 1 : 2000 mol mol^{-1}.

	Modifier	X (%)	S (%)	IP (%)
1	None (pure DIP)	100.0	13.0	13.0
2	THF 	100.0	22.8	22.8
3	Dipropyl sulfide 	100.0	26.7	26.7
4	Furan 	98.7	32.5	32.1
5	Quinoline 	100.0	59.2	59.2
6	Ethyl-2-hydroxyethyl sulfide 	100.0	63.7	63.7
7	Tetrahydrothiophene 	100.0	67.0	67.0
8	Thiophene 	98.9	75.9	75.1
9	Diethylaminoethanol 	96.8	84.3	81.6
10	Propyl disulfide 	96.6	88.7	85.7
11	Isopropyl disulfide 	88.3	95.5	84.3
12	2,2′-(ethylendioxy)-diethylamine 	72.9	90.7	66.1
13	2,2′-(ethylendithio)-diethanol[a] 	49.4	97.2	48.0
14	2,2′-(ethylendioxy)-diethanthiol 	3.7	100.0	3.7

[a] Proposed in [17].

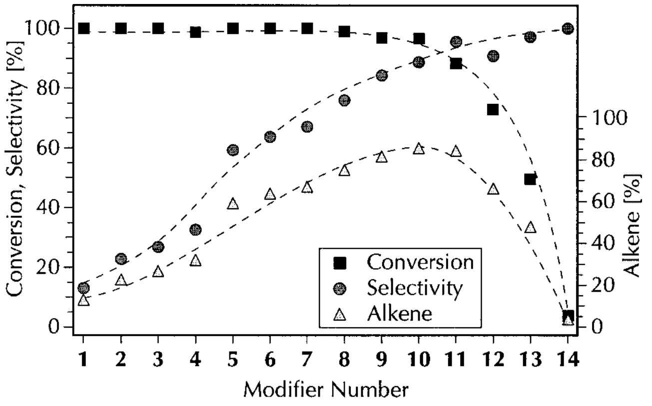


Figure 3. Influence of different modifiers on conversion and selectivity of the reaction: **1** – no modifier, **2** – THF, **3** – dipropyl sulfide, **4** – furan, **5** – quinoline, **6** – ethyl-2-hydroxyethyl sulfide, **7** – tetrahydrothiophene, **8** – thiophene, **9** – diethylaminoethanol, **10** – propyl disulfide, **11** – isopropyl disulfide, **12** – 2,2′-(ethylendioxy)-diethylamine, **13** – 2,2′-(ethylendithio)-diethanol, and **14** – 2,2′-(ethylendioxy)-diethanthiol.

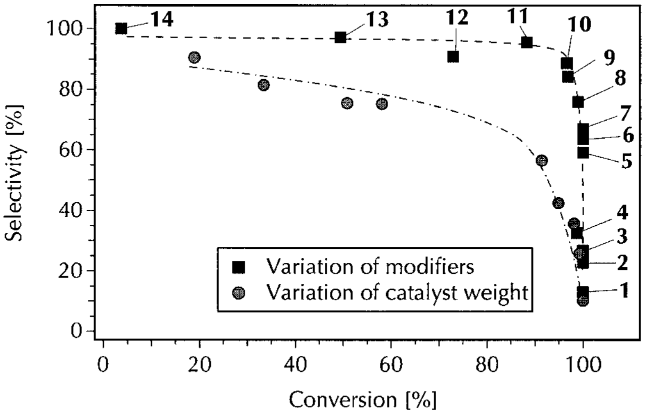


Figure 4. Comparison of the results obtained by employing different modifiers with the data from an experiment where the catalyst amount was varied shows that the influence of the modifiers on the selectivity is significant, and not just a result of decreased conversion in presence of the modifier.

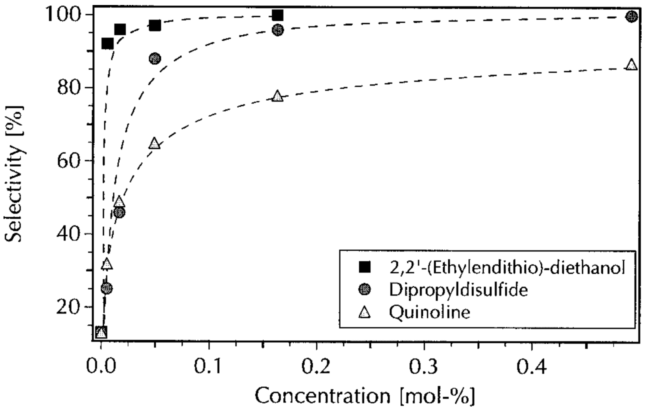


Figure 5. Effect of modifier concentration in the feedstream during semihydrogenation of DIP.

employed in this work and on the corresponding activities, selectivities, and IP-yields obtained. Most molecules were similar to 2,2′-(ethylendithio)-diethanol in one way, *viz.* containing sulfur heteroatoms, or the other, *viz.* showing structural analogies. Additionally, the effects of quinoline, THF and furan were considered.

For a better overview, conversion and selectivity values, obtained by the use of the various modifiers, are also graphically compared in figure 3. All experiments were conducted consecutively with a 4 h run without modifier in between. Modifier poisoning proved to be completely reversible in each case. All modifiers improved the selectivity which was *ca.* 13% without modifier. Depending on the specific modifier, the new selectivities ranged from 23% (THF) to 100% (2,2′-(ethylendioxy)-diethanthiol). The highest selectivities, however, were accompanied by a strong decrease in activity, being, *e.g.*, as low as 3.7% for 2,2′-(ethylendioxy)-diethanthiol.

In order to show that the increased selectivity is not only a consequence of a lowered conversion (as would be expected for a plug-flow reactor), the above obtained selectivity *vs.* conversion data were compared to a reference experiment without addition of modifiers (figure 4). The latter was recorded by subsequently increasing the mass of catalyst, and thus the w/F ratio from 5 to 70 g s mol^{-1}. Clearly, a difference of more than 30% remains for a broad range of conversion values which must be attributed to the effect of the modifiers.

In figure 5 the concentration dependence of the selectivity was investigated for three of the modifiers (quinoline, propyl disulfide, and 2,2′-(ethylendithio)-diethanol) by increasing the amount of modifier in the reactant stream each 6–12 h. For the most effective modifier (2,2′-(ethylendithio)-diethanol) even smallest concentrations (as low as 0.005 mol%) led to a significant increase in selectivity, whereas for propyl disulfide and especially for quinoline larger amounts were required in order to reach a similar effect. In analogy to figure 3, higher selectivity was always accompanied by decreasing conversion (not shown in figure 5).

Additionally, the concerted effect of two modifiers (quinoline, **5**, and 2,2′-(ethylendithio)-diethanol, **13**, each 1 : 2000 mol mol^{-1}) was explored. While quinoline alone resulted in a significant increase of selectivity, it could not further improve the selectivity of the pure 2,2′-(ethylendithio)-diethanol modifier after combined addition of both modifiers to the DIP feed.

3.2. Lead-modified catalyst

In figure 6 various selectivity *vs.* conversion data points for the lead-modified catalyst (pure and in combination with organic modifiers) are compared to corresponding measurements on the Pb-free catalyst (see figure 4). For a better comparison, the lines from figure 4 were added. The main effect of Pb was to decrease the activity of the catalyst, while the selectivity improvement at a given conversion was only minor compared to the effect of the pure organic modifiers.

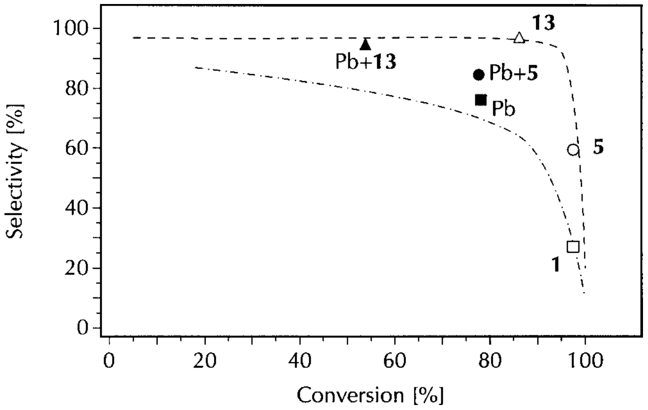


Figure 6. Influence of Pb and organic modifiers. **1** – no modifier, **5** – quinoline, **13** – 2,2′-(ethylendithio)-diethanol, and all in combination with Pb. Catalyst mass of unmodified $Pd_{81}Si_{19}$: 5 g, catalyst mass of Pd-modified $Pd_{81}Si_{19}$: 3 g. Additionally, the lines from figure 4 are shown for comparison.

4. Discussion

All organic modifiers improved the selectivity, however, at the expense of a lowered conversion. Nevertheless, the selectivity at a given conversion is improved considerably by the presence of such additives. From the comparison of the different modifiers it can be concluded that molecules containing a higher number of heteroatoms exhibit a stronger effect on selectivity (and also conversion). The presence of conjugated double bonds amplifies the effect of the modifier, probably because they further strengthen bonding to the catalyst surface (*e.g.*, tetrahydrothiophene *vs.* thiophene). Additionally, a strong dependence of the selectivity on the nature and position of the heteroatoms (S, O, or N) could be observed. The latter effect, however, seems also to depend on the specific structure of the modifier and cannot be generalized (compare, *e.g.*, ethyl-2-hydroxyethyl sulfide *vs.* diethylaminoethanol and 2,2′-(ethylendioxy)-diethylamine *vs.* 2,2′-(ethylendioxy)-diethanthiol). Moreover, even small changes in the structure, without changing the heteroatom, can lead to significant effects, as is demonstrated with propyl disulfide *vs.* isopropyl disulfide.

In order to gain a maximum IP yield, a compromise between high selectivity and reasonable conversion is important. Under this aspect, propyl disulfide and isopropyl disulfide represent the best choices for the applied conditions (figure 4). However, the selectivity cannot only be tuned by choosing the appropriate modifier, but also by adjusting the concentration of the latter.

Several mechanistic models have been put forward in order to explain the selective poisoning by organic modifiers, including a restructuring of the Pd surface induced by organic modifiers [3,5] or a site-blocking of the most active (and hence least selective) sites by modifier molecules [18,19]. Alternatively, a recent study by Yu and Spencer suggested a model which also includes competitive adsorption of reactants and the modifier, but attributed the effect to an electronic modification of the neighboring Pd sites by the adsorbed modifier [20].

In this study we observed that (i) a large variety of modifier molecules (differing in structure and heteroatoms) in each case exhibit a similar effect (of different extent, however), (ii) the effect was fully reversible after stopping the modifier addition and continuing with pure DIP, (iii) the magnitude of the effect was strongly influenced by the modifier concentration, yielding a saturation-type curve (figure 5), and (iv) when adding two modifiers, the one with the stronger impact clearly governs the overall effect.

These findings fit very well with a model including competitive adsorption of reactants and modifier molecules, where the latter are most strongly adsorbed on the catalyst surface. Compounds having a higher adsorption energy on Pd are expected to result in larger modifier coverages, and hence should show the strongest impact on selectivity (and activity). This is reflected by the fact that molecules with a larger number of heteroatoms, which most probably represent the anchoring point to the catalyst surface, afford higher selectivities. On the other hand, the large chemical variety of effective modifiers does not comply with a surface restructuring model, since it appears unlikely that each employed molecule induces similar restructuring. Finally, our results do not allow to distinguish between a simple site-blocking and a secondary alteration of the electronic properties of the surface. The significant difference in the effects of the structural isomers, propyl disulfide and isopropyl disulfide, however, implies that, at least partly, steric effects are involved.

Nevertheless, it cannot be excluded that an additional contribution to the modifier effect may arise from the imaginable suppression of the palladium hydride formation which was shown to be maleficent to the semihydrogenation of, *e.g.*, acetylene [21]. Further measurements, required in order to fully unravel the true nature of the selective poisoning by organic modifiers, are currently under investigation.

In numerous studies lead has been employed as an inorganic modifier to increase the selectivity for the semihydrogenation of acetylenes (*e.g.* [1,22]). Here, we found that lead alone does not increase selectivity as much as organic modifiers (*ca.* 5% as opposed to as much as 30%). A significant increase in selectivity can only be observed in combination with an organic modifier. When lead is combined with 2,2′-(ethylendioxy)-diethanthiol, the selectivity is about the same as with 2,2′-(ethylendioxy)-diethanthiol alone, but at significantly lower conversion (figure 6). Thus, the application of organic modifiers is crucial for achieving high selectivity in the continuous semihydrogenation of DIP over amorphous $Pd_{81}Si_{19}$ in dense CO_2.

The effect of dense CO_2 on the catalytic performance seems to be mainly restricted to enhancing mass transfer, as emerged from the parallel study of the relationship between phase behavior and catalytic performance reported elsewhere [15].

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