

Hydrogenation of carbon–carbon multiple bonds: chemo-, regio- and stereo-selectivity

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Abstract

Results of the last decade with respect to the selective hydrogenation of hydrocarbons with multiple unsaturation (dienes and alkynes) over heterogeneous palladium catalysts are reviewed. Factors such as metal dispersion, carbon deposits, and the use of promoters and additives controlling catalytic activities and chemo-, regio- and stereo-selectivity are discussed. A detailed treatment of the status of the selective removal of hydrocarbon impurities with multiple unsaturation from industrial feedstocks is also given. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Selective hydrogenation of hydrocarbons with multiple unsaturation, i.e. dienes and acetylenes (alkynes), to achieve partial hydrogenation and, therefore, to synthesize monoenes is of fundamental importance. The selective synthesis of alkenes by catalytic hydrogenation is widely used in both laboratory practice and fine chemicals production. It is also a crucial step in industrial polymerization processes with the aim of the complete elimination of alkynes and dienes from alkene feedstocks. Specifically, the selective hydrogenation of acetylene in ethylene-rich stream (C2 hydrorefining), and similarly, the selective removal of propyne and propadiene from propylene-rich stream (C3 hydrorefining) are to avoid poisoning of the polymerization catalysts. Naturally, high ethylene and

propylene yields, respectively, are required without hydrogenating the existing alkene. In the same line, removal of residual 1,3-butadiene from C4 raw cuts (C4 hydrorefining) is also a catalytic process of vital importance to produce either 1-butene (for polymerization) or 2-butene (for alkylation).

C2–C4 alkenes and reactive intermediates, such as ethylene oxide, vinyl chloride, propylene oxide, acrylonitrile, etc., are the most important building blocks in the modern petrochemical industry. In 1950 the world ethene production just reached 1 million tons per year [1]. The high importance of this chemical is clearly indicated that its production reached 80.5 million tons in 1998 [2,3]. Polypropylene, one of the fastest growing commodity thermoplastic resins, created a strong demand on propylene. In 1998, the world capacity reached 47 million tons and the global PP production (in 1996) was already 22 million tons [4]. The annual growth is 3.5% for ethylene and more than 5% for propylene production. For 2010, the worldwide demand is predicted to reach 120 and 82 million

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tons per year for these alkenes, respectively. The larger molecular weight alkenes (1-butene, 2-butenes, isobutylene and isopentene) are also highly valued feedstocks used in polymerization, alkylation, methyl *tert*-butyl ether (MTBE) and *tert*-amyl methyl ether (TAME) production, oxo synthesis, etc. [5].

The topic of selective hydrogenations has been extensively studied and covered in books [6–10] and review papers [11–14] since the 1960s. There is, however, an unflagging interest to develop more selective catalysts and an intense research activity is still continuing to provide better understanding of the factors, which are decisive in governing selectivities. A large body of work has been, therefore, published in recent years and the topic is again the subject of recent reviews [15–20] which further underlines the significance of these transformations.

The present review is intended to collect and analyze the results with respect to the use of heterogeneous palladium catalysts in the selective hydrogenation of alkynes and dienes disclosed in the last decade. An attempt will also be made to summarize our present knowledge and understanding of the various factors controlling activity and selectivity phenomena of the palladium-catalyzed selective hydrogenation processes. Relevant data from the 1970s and 1980s are also cited in the interpretation when necessary.

2. The problem of selectivity

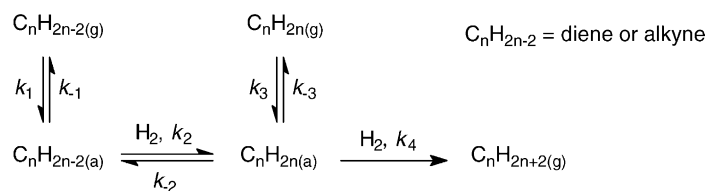
The regioselective hydrogenation of a diene or the chemoselective hydrogenation of an acetylene to form the corresponding monoene is called semihydrogenation or half-hydrogenation. It is well known that many heterogeneous metal catalysts exhibit high activity in the hydrogenation of the carbon–carbon double and triple bond. However, palladium appears to be by far the most selective metal to achieve selective

semihydrogenations. In addition, it is also capable of transforming non-terminal alkynes to *cis*-alkenes with very high selectivity.

A general scheme of hydrogenation of hydrocarbons with multiple unsaturation, the so-called ‘rake’ mechanism, is given in Scheme 1 [21–23].

For the intermediate monoalkene, two kinds of selectivity can be defined. Selective formation of an alkene can be expected if $k_2 \gg k_4$ (mechanistic selectivity). On the other hand, if $k_1/k_{-1} \gg k_3/k_{-3}$, then the adsorption of the polyunsaturated molecule prevents the readsorption of the alkene and hence the consecutive hydrogen addition cannot take place (thermodynamic reason of the selectivity). All experimental observations indicate that Pd exhibits the highest selectivity for semihydrogenation. Over Pd the rates of saturation of one double bond of alkynes or dienes, and the subsequent hydrogenation of the product alkene have usually the same order of magnitude. Selectivity, therefore, is attributed to the stronger adsorption of the diene/alkyne compared to that of the monoene formed [22–27]. Data in Table 1 show that adsorption coefficients of alkynes and dienes are always higher [28,29]. This results in the preference of their hydrogenation in competitive hydrogenations although, as individual substrates, they are hydrogenated slower than alkenes.

The above model offers a sound basis for the interpretation of the high intrinsic selectivity of palladium. Findings in the 1970s and 1980s showed, however, that the selectivity of alkene formation cannot be interpreted without the detailed knowledge of the reaction mechanism and the actual surface state of the working Pd sites. Consequently, considerable attention has been focused on the formation of various surface intermediates and on the role of controlling factors such as dispersion, modifiers and promoters with the principal objective to increase the selectivity of alkene formation.



Scheme 1.

Table 1
Selectivities ($S_{A,B}$) of competitive hydrogenations^a, reaction rates and adsorption coefficients (K_A/K_B) [28,29]

Substrate		$S_{A,B}$		k_A/k_B^b		K_A/K_B	
A	B	Pd	Pt	Pd	Pt	Pd	Pt
1-Hexyne	1-Octene	16.0	4.7	0.12	0.13	133.3	36.2
1-Hexyne	1-Heptene	15.0	4.7	0.13	0.15	115.4	31.3
1,7-Octadiene	1-Hexene	2.5 (2.79) ^c	1.4	0.64 (0.44)	0.49	3.90 (6.34)	2.8
1,7-Octadiene	1-Heptene	2.4 (2.62)	1.8	0.67 (0.43)	0.53	3.6 (6.09)	3.4
1-Hexyne	1,7-Octadiene	6.5	3.0	0.19	0.28	34.2	10.7

^a 3% Pd-on-C, 293 K.

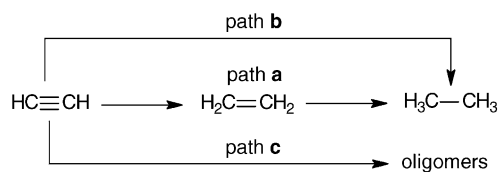
^b k_A and k_B are initial reaction rates determined in the hydrogenation of individual substrates.

^c Data in parentheses were determined in transfer hydrogenation.

3. Hydrogenation of alkynes

Hydrogenation of alkynes over palladium leads to the selective formation of the corresponding alkenes. The reasons for this phenomenon are still not fully understood but, according to the classical interpretation, activity and selectivity are essentially governed by thermodynamic effects, i.e. by the specificity of the interaction of the metal sites with various carbon–carbon multiple bonds. Specifically, it is attributed to the strong adsorption of alkynes compared to that of alkenes. Indeed, it was found by studies in ultra-high vacuum that acetylene adsorbs more strongly than ethylene [30]. Due to the higher adsorption enthalpy of the alkynes, the ratio of surface coverages of an alkyne and an alkene remains very high until virtually all alkyne disappears. This means that the alkyne either displaces the alkene from the surface or blocks its readsorption. As a consequence, an alkene is not hydrogenated in the presence of an alkyne, while it undergoes ready hydrogenation in the absence of the alkyne.

Studies in the late 1970s showed, however, that ethylene hydrogenation occurred even at high acetylene partial pressures [31,32]. Involvement of different reaction sites was suggested: on a fraction of sites acetylene was selectively hydrogenated to ethylene whereas on the other, non-selective sites ethylene was hydrogenated even in the presence of acetylene. ¹⁴C labeling experiments showed the existence of an additional, direct route from acetylene to ethane [32–34]. The mechanism of acetylene hydrogenation to produce either ethylene or ethane, therefore, proceeds via two paths (Scheme 2) [10,20,32].



Scheme 2.

Path **a** is the hydrogenation of acetylene to ethylene followed by desorption and readsorption of ethylene and further hydrogenation to ethane. Path **b**, in turn, is the reactive adsorption of acetylene to produce multiple bound intermediates, which are directly hydrogenated to ethane. The relative significance of the two paths and, therefore, selectivity can be controlled by the catalysts and the reaction parameters. The morphological properties of the working catalyst appear to strongly affect the overall pattern of selectivity.

The consecutive–parallel route of acetylene transformation presented above is not complete yet since one has to consider oligomerization/polymerization of acetylene (path **c**) leading to the formation of hydrocarbons of even carbon numbers ranging from C4 to C32. Studies at subatmospheric and atmospheric pressures have reported 20–40% C4+ selectivity and the first oligomers (butenes and 1,3-butadiene) are always present among the products formed. The high selectivity for oligomer formation is a peculiar feature of acetylene. With increasing substitution, the selectivity of oligomer formation decreases due to steric interferences in the C–C bond forming step.

Various observations acquired mainly by surface science techniques (FT-IR, EELS, SFG, HREELS, ARUPS, etc.) combined sometimes with kinetic

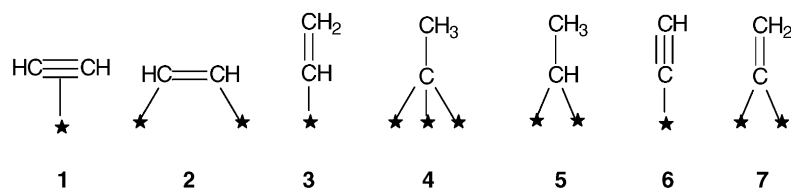


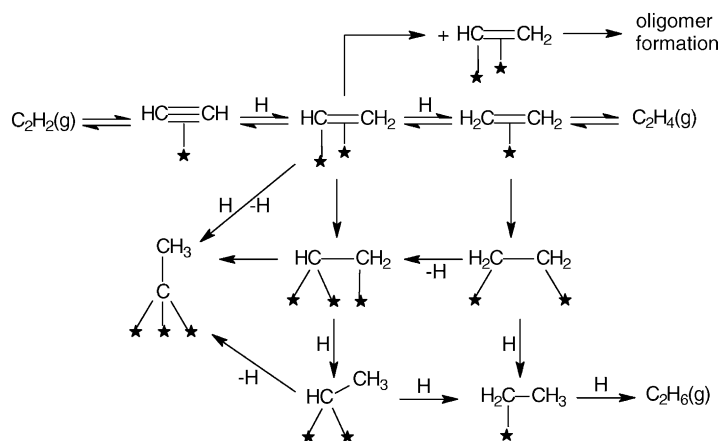
Fig. 1. Proposed surface intermediates in hydrogenation of acetylene.

studies allowed to postulate the possible adsorbed species participating in the above processes. π -Adsorbed acetylene (**1**) is transformed to associatively adsorbed (di- σ -adsorbed) flat-lying acetylene (**2**), then to vinyl species (**3**) which are the precursors for the formation of ethylene (Fig. 1). Multiply bound surface intermediates such as ethylidyne (**4**) and ethylidene (**5**) are hydrogenated to ethane. Dissociatively adsorbed acetylene (**6**) and vinylidene (**7**) were suggested to participate in forming oligomers and benzene [35]. Recently, however, species **7** was also assumed to be the reactive intermediate in ethylene formation [36–40]. One must note, however, that some of these species were identified under UHV conditions which in no way means that they appear under atmospheric conditions. FT-IR, SFG and deuterium labeling (location of the D position) are of crucial importance in interpreting the formation of reactive and spectator species. These techniques verified the presence of species **2**, **4** and **6**.

Formation of C4 has been investigated to the same extent. Angle resolved ultraviolet electron

spectroscopy (ARUPS) seems to provide evidence that the C4 unit is formed from vinylidene or flat lying acetylene. The C4 unit remains adsorbed as a tilted metallocycle. Under UHV conditions, benzene can also be detected but cyclotrimerization is sensitive to hydrogen pressure and rapidly suppressed with the formation of deposits. Benzene is observed to lay flat at low coverages but it becomes tilted at high coverages. It can also be noted that benzene formation is only a side reaction in the formation of oligomers observed at atmospheric hydrogenations since after C6 ring closure further insertion of the C2 unit is terminated [30,35,41–44]. Reaction paths leading to all possible product and the corresponding surface intermediates are summarized in Scheme 3. It is to be noted that only π - and $\sigma\pi$ -bonded species are involved in ethylene formation.

Due to its significance in the petrochemical industry, a large body of work has accumulated about the hydrogenation of the parent compound acetylene. In contrast, much less information is available on the higher homologues, although the hydrogenation of



Scheme 3.

propyne is of similar practical importance. Moreover, a recent paper has shown that acetylene is a rather special case and cannot be used as a general model for the hydrogenation of higher alkynes [45]. Replacement of C–H with C–R decreases the strength of alkyne interaction with the surface due to increased substrate–surface repulsion which also hinders hydrogen addition. In addition, certain intermediates such as alkylidyne or alkylidene may not be formed from internal acetylenes.

Most studies in recent years have focused on the use of supported palladium catalysts. Pd-on- Al_2O_3 [46–61], Pd-on- SiO_2 [46,49,50,53–55,62–64], Pd-on- ZrO_2 [49], Pd-on-C [29,45,54,65], Pd-on-pumice [50,59,66,67], Pd-on-sepiolite [68–70], Pd-on- CeO_2 [71], and palladium supported on mesoporous (K10 montmorillonite, MCM-41) and microporous materials (Y zeolite) [72], and polymers [54,73] were applied. Polycrystalline bulk Pd samples were also shown to be good model catalysts for studying acetylene hydrogenation [35,74]. The compounds studied included acetylene [35,46,53,62,63,74], methylacetylene [45,49,51,64], phenylacetylene [45,54,55,65–70,72,73], other terminal alkynes [29,45,47,48,68,71,73], and internal alkynes [45,68,72,73,75]. Due to the practical significance numerous studies were conducted with acetylene or methylacetylene in, respectively, ethylene or propylene-rich feedstock [50,52,56–61,76].

The main objective in the hydrogenation of alkynes is to achieve the highest possible alkene selectivity. Most of these studies, therefore, focus on the role of various factors, namely, operating conditions, metal dispersion, carbon deposits, promoters and additives on semihydrogenation selectivity. Kinetic studies to give rate equation are rather scarce [20,76–82] and they are usually able to describe the hydrogenation process for a rather narrow range of reaction conditions. This is not surprising and can be attributed mainly to the high complexity of these reactions occurring simultaneously on the catalyst surface (competitive hydrogenation, oligomer and deposit formation).

3.1. *Effect of dispersion on activity and selectivity*

The effect of particle size on the catalytic properties of supported metals is an important problem in heterogeneous metal catalysis [83,84] and still the

subject of systematic studies. Changing the dispersion, i.e. the particle size of the metal may affect both specific activity (turnover frequency, TOF) and selectivity. These changes are believed to be brought about by electronic and geometric effects [85–87]. When atoms surrounding a metal atom on the surface are replaced by other atoms, this will change the nature of chemisorption bond. This is called electronic or “ligand effect”. It is also known that electronic properties of metal particles can change appreciably when the number of atoms in an isolated metal particle is reduced. There is much evidence to indicate that very small metal particles do not have the band structure characteristic of bulk metals and they appear to be electron deficient [88,89]. Chemisorption of electron-rich substrates such as alkynes (and dienes) will, therefore, be affected. The relative ratio of various types of surface atoms, on the other hand, does also change substantially with varying particle size. Large particles possess mainly large crystal planes with atoms of high coordination number (terrace atoms), whereas metal atoms with low coordination numbers (edge and corner atoms) are characteristic of small particles. Reactions that require the largest ensembles are affected most. Such changes may manifest themselves as geometric or “ensemble effect”.

The results of various studies in the 1980s with respect to particle size effects of the transformation of alkynes are rather controversial, although most studies showed that alkyne hydrogenation is a structure sensitive reaction at high dispersions. Strong antipathetic behavior was observed, i.e. increasing metal dispersion was found to bring about a decrease in specific activity [90–93] especially over catalysts with small particle size (Fig. 2). On the other hand, small particles of a medium dispersed Pd-on- Al_2O_3 catalyst exhibited slightly higher activity [94]. Recent publications have disclosed structure insensitivity [53,55] or only small changes in activity [66,67,95], but activity drops with increasing dispersion were also reported [48,50,56,61,71] (Fig. 2). Direct comparisons of the results, however, are difficult since different substrates were studied under different reaction conditions. Nevertheless, strong complexation of the highly unsaturated alkyne to atoms of low coordination number on small metallic particles is usually invoked to explain the diminishing activity of small metal particles [87,90,91,93,96].

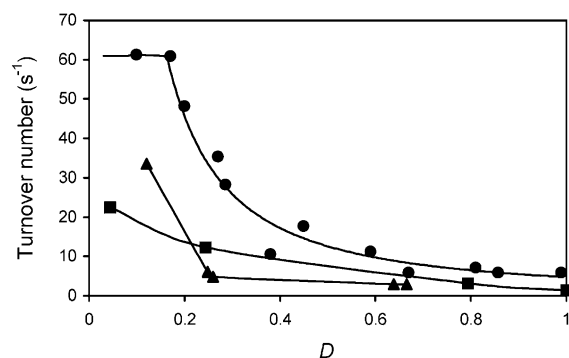


Fig. 2. Variation of turnover numbers as a function of dispersion in the hydrogenation of 1-butyne. (●) Pd-on-Al₂O₃ [91], (▲) Pd-on-pumice [50], (■) Pd-on-CeO₂ (data taken from [71] were multiplied by 10).

With respect to selectivity changes some of the earlier [90,91] and recent results [51,55,66,67,71] indicate that catalysts with low dispersion (higher particle size) ensure better selectivities for alkene formation. In other cases no effect was observed [48,50,56,61,66,67,92,93]. It must be emphasized, however, that the problem of selectivity cannot be discussed independently from the question of hydrocarbon deposits since these have been found to have a profound effect on the alkene formation selectivity. As opposite to that, Poncic argues that the particle size variation (decrease in selectivity with increasing dispersion) is an apparent one [62] and the particle size effect disappears in repeated runs.

In earlier studies, selectivity changes were frequently interpreted in terms of hydrogen availability and the over-hydrogenation was attributed to the presence of β -PdH phase whose formation was evidenced in some of these studies by XRD [97,98].

The probability of formation of the palladium β -hydride phase is, however, known to decrease with increasing dispersion. The highly selective alkene formation over highly dispersed catalysts, therefore, was regarded as evidence to show that the β -hydride does not participate in the hydrogenation process [79,99,100]. The role of β -hydride phase in over-hydrogenation is still questionable. One has to consider that the hydride phase decomposes when H₂ is removed from the reactor by He treatment or evacuation. In the presence of alkyne–hydrogen mixture, the reacting alkyne monopolizes the Pd sites ensuring

thereby the large alkene selectivity. Hydrogen atoms formed by dissociation in a non-competitive process are almost immediately consumed by the formation of alkene. One might expect, therefore, that under conditions of selective semihydrogenation, the surface fugacity of hydrogen might not be high enough to ensure formation of β -PdH. It is tempting to suggest that formation of β -PdH is the consequence of non-selective working of the sites, which permits β -PdH formation at large hydrogen pressures. It can also be noted that high alkene selectivity was also reported in the presence of hydride phase and in a recent study, the detrimental effect of β -PdH was not observed [74]: ethylene selectivity remained low under the reported conditions both in the presence and in the absence of β -PdH. In other H₂ consuming reactions such as methyl- and ethyl-cyclopropane hydrogenative ring opening, lower rates were observed in the presence of the β -hydride phase [101,102]. Although the reaction requires hydrogen, apparently the adsorption of these molecules does not facilitate the decomposition of β -PdH.

3.2. Effect of carbon deposits

It has long been known that strongly held residues so-called carbon deposits, also referred to as hydrocarbon or carbonaceous overlayer, are formed during the hydrogenation of hydrocarbons [103–105].

Al-Ammar and Webb in a series of papers presented strong evidences using ¹⁴C tagged hydrocarbons that both acetylene and ethylene adsorb in two stages [32,106]. They suggested that in the first stage irreversible dissociative adsorption occurs, while in the second stage, acetylene and ethylene adsorb and react upon the catalyst covered by the primary layer. In 1976, Thompson and Webb took up a line that highly dehydrogenated C_xH_y species formed in the early stages of hydrogenation can be regarded as hydrogen source which plays a crucial role in the hydrogenation process [107].

When alkynes are hydrogenated the accumulation of residues is often manifested in a non-steady-state initial period and a decline in catalytic activity. Using the pulse-flow technique Jackson and Casey showed in hydrogenation of propyne that during non-steady-state regime, a significant amount of carbon builds up on the catalysts resulting in Pd:C ratios

of 1:3 for Pd-on-ZrO₂ and Pd-on-SiO₂, and 1:50 for Pd-on-Al₂O₃ [49]. In the non-steady-state regime the formation of deposits exceeded propene formation and selective propene formation could only be observed after this initial break-in period. Similarly, pulse experiments with acetylene over Pd-on-SiO₂ in hydrogen stream have confirmed the formation of irreversibly bound species even at 273 and 298 K which, in TPO experiments, desorbed as CO₂ at 403 and 423 K, respectively [108].

Alkynes, however, especially acetylene, readily undergo polymerization as well. In the hydrogenation of acetylene, both gas phase oligomers (C₄–C₈) and heavier hydrocarbons (C₈+) are formed. The liquid part of the oligomers (C₈+), often referred to as “green oil”, appears downstream. Surface oligomers/polymers, which remain on the catalyst under the reported conditions, are frequently regarded as coke or deposit and referred to as the carbon content of the catalyst. Depending on the conditions of operation, a considerable fraction of surface oligomers/polymers can be removed by solvent extraction or hydrogenation treatment at elevated temperatures indicating that the low vapor pressure keeps some of the oligomers in the pores at the temperature of the hydrogenation. Composition of the oligomers extracted from spent catalysts is shown in Fig. 3. The less reactive part of the surface oligomers can only be removed by O₂ treatment to regenerate the catalytic activity.

Oligomers formed in acetylene hydrogenation consist of different alkenes, dienes and, to a lesser extent, alkanes of even carbon atoms with little branching and an H:C ratio of about 1.9 [20]. Yayun

et al. have reported that under industrial conditions the mean molecular weight of oligomers isolated after 427, 5300 h and 1 year in operation was 196, 220 and 231, respectively [110]. The ratios for aromatic-H:alkyl-H, olefinic-H:alkyl-H and α-olefinic-H: internal olefinic-H were claimed to be 0.008, 0.08 and 0.21, respectively, after 5300 h in operation.

There are diverging results concerning the effect of temperature and H₂:C₂H₂ ratio on the selectivity of the oligomers. Yayun et al. found that increasing acetylene pressure increases oligomer formation while the temperature played no significant role [110]. Gandman et al. observed no effects at H₂:C₂H₂ ratios between 3 and 7 [111], whereas Yayun reported suppression of oligomerization in the interval 1.5–4. Oligomer formation is connected with hydrogenation which is indicated by the fact that hydrogen is a necessary requisite for oligomer formation [112] and in its absence, oligomers were not observed.

As far as the mechanism of oligomer formation is concerned, in principle, C–C bonds might be formed by recombination of neighboring intermediates or by insertion of a C₂ unit into an existing Pd–C bond. Sheridan [113] and later Bond and Sheridan [114] proposed participation of free-radical type vinyl intermediate in the oligomer formation. In recent studies, ICI coworkers [115,116] using spin-trapping technique have confirmed the presence of radicals, although the origin of these species are not entirely clear yet. If a radical mechanism were operative, one would expect recombination of a C₂ radical and ethylene arriving from the gas phase. Studies with acetylene and propene mixtures or the results with tagged acetylene seem to suggest that the oligomer arises entirely from acetylene. The C₄ formation observed by Kemball et al. as a second order reaction with respect to acetylene partial pressure may support direct recombination [31]. UHV studies mentioned earlier [36–40] interpret C₄ formation by recombination of neighboring vinylidene.

CO used frequently as stream additive has been observed to incorporate in the oligomers resulting in the formation of carbonyl compounds (aldehydes, acids), suggesting that for CO, the insertion mechanism is certainly operating [115–117]. CO insertion into Pd–C terminates the addition of further C₂ units. Moreover, as observed in oxo synthesis, the probability of CO insertion into α-alkenes decreases with increasing

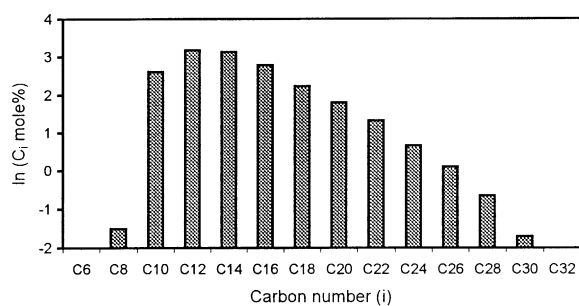


Fig. 3. Molar distribution of soluble surface polymer extracted from spent catalyst samples in 2-methylpentane [109].

carbon chain. Acids are formed with the contribution of surface OH groups on the support.

Coke formation may result in both decreasing and increasing activities and selectivities depending on the catalyst (metal loading, properties of the support) and operating conditions (hydrogen pressure, alkyne:hydrogen ratio). The mechanism of coke formation is still a research field not entirely clarified yet. It is likely, however, that the very unreactive deposits are formed from multiple adsorbed species or reactive oligomers upon losing hydrogen.

Accepting that the Pd sites are almost immediately covered by hydrocarbonaceous residues (trapped hydrocarbon species, oligomers and deposits), the question to be answered is how the catalytic sites are affected by carbonaceous materials. It is clear that the conditions of operation and duration of experiments affect the carbon content which, in turn, influences the interpretations.

The hydrocarbon overlayer is usually considered to be adsorbed irreversibly on the metal surface. Boitiaux et al. [118] considering self-inhibition and structural dependence for 1-butyne hydrogenation have arrived at the conclusion that the phenomenon might be caused by the complexation and subsequent deactivation of a single metal atom by two butyne molecules. This can be described formally as in Eq. (1), and then the surface concentration of the inactive sites is given by Eq. (2) (BY stands for 1-butyne).



$$\sigma_{\text{BY}2} = K' \sigma_{\text{BY}} c_{\text{BY}} \quad (2)$$

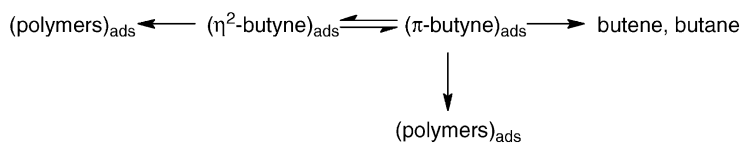
Recently, Touroude and Maetz [47] have presented evidence acquired by transient methods and FT-IR that a less reactive hydrocarbon species may be responsible for the selectivity in the hydrogenation of 1-butyne over Pt and Pd. During the initial phase of the catalytic process, both reactive and less reactive surface species are formed. Based on FT-IR, they assigned the

less reactive species to η^2 -butyne species in addition to irreversible hydrocarbon residue and the reactive, π -bonded butyne species (Scheme 4).

The authors conclude that hydrogenation requires π -bonded butyne whereas the η^2 -butyne species, although it can be removed from the surface in large excess of hydrogen, may not be reactive enough at low H_2 :HC ratios. The η^2 -butyne species is supposed to be in equilibrium with the reactive intermediate. The above interpretation is in line with conclusions by Somorjai et al. which emerged from hydrogenation of ethylene and propylene studied at atmospheric pressure over Pt(111) by SFG [119–121]. On an originally clean surface, a weakly bound reactive intermediate appears after all the strongly bonding sites are occupied. Hydrogenation proceeds then in such a way that the strongly adsorbed species are compressed into a more compact layer which leaves room for the adsorption of the reacting hydrocarbon. Until further proofs, this model is likely to be valid for alkyne hydrogenations as well.

Many different explanations have been put forward to interpret the effect of carbonaceous deposits located on the metal surface. In line with the original suggestion [107], Webb argues that hydrogenation of acetylene takes place on top of the irreversibly adsorbed carbon-rich first layer [104]. This layer serves as a hydrogen transfer agent to supply hydrogen from the underlying palladium to the alkyne adsorbed in the second layer. Detailed studies with ethylidyne have convincingly shown that this species due to its low reactivity behaves as a spectator in ethylene hydrogenation and cannot serve as hydrogen donor. Deuterium exchange taking place in parallel with hydrogen addition was found to be different on each metal indicating the adsorption of the reactive species directly on the metal. These observations question the validity of the explanation put forward by Webb [107].

Ponec et al. also offered a different explanation to disprove the direct involvement of the carbon layer in



Scheme 4.

hydrogenation [62,63]. They suggest that the drop of activity during the initial stage of the reaction testifies to the inactivity of the carbonaceous overlayer. Its ability to modify selectivity is explained by the ensemble size effect [85]. Large ensembles are able to form multiple metal–carbon bonds and, therefore, are probably sites for the formation of ethane via strongly bound intermediates, i.e. responsible for low selectivity. Carbon deposition, in turn, diminishes the average ensemble size of the active metal available for the reaction. Such smaller ensembles bind acetylene less strongly resulting in the suppression of dissociatively adsorbed, possibly multiple bound species. The formation of ethane, therefore, is suppressed resulting in a higher selectivity to ethylene.

In a thorough study by Deganello et al., the activity of Pd-on-pumice catalyst in hydrogenation of acetylene was interpreted by a specific electronic metal–support interaction [59]. Electron density of the metal is suggested to govern activity by changing the oxidation properties of the metal and surface–reagent interactions. It also affects the formation of surface hydrocarbon deposits thereby influencing selectivity. Low hindered sites accessible to all reagents and poisoned sites coated by carbonaceous deposits not accessible to any reagents are suggested to exist on the surface. Poisoned sites interacting with neighboring sites do generate high hindered sites which become accessible only to acetylene and hydrogen and, therefore, are selective in yielding the alkene. Polymeric or other species of low reactivity, which are occupying active sites and thereby inhibiting the adsorption of the intermediate alkene, were proposed to account for the high selectivity in the hydrogenation of phenylacetylene over the same catalyst [66,67]. It was also suggested that large Pd particles are easily poisoned by phenylacetylene and as a consequence of combined poisoning and electronic effects the catalytic activity (TOF) becomes almost independent of dispersion. The carbonaceous layer was also supposed to affect selectivity through a ligand donor effect, which causes a diminution of the adsorption strength of unsaturated molecules favoring the selectivity towards the alkene [55].

The effect of hydrocarbon deposits on catalytic activity and semihydrogenation selectivity has been widely studied in hydrogenation of acetylene due to the great practical importance. In these experiments,

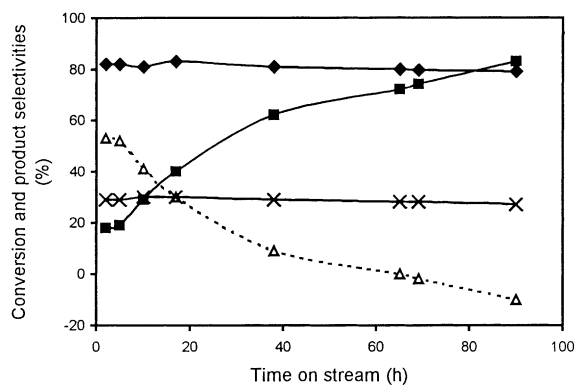


Fig. 4. Effect of aging on product selectivities in the hydrogenation of a tail-end mixture over Pd-on- γ -Al₂O₃ [122]. (◆) conversion, (▲) ethylene selectivity, (■) ethane selectivity, (×) C4+ selectivity.

the hydrogenation runs for several hours and, therefore, the carbon loading of these catalysts becomes very high reaching sometimes many hundred mg of deposit/ml pore volume. Time on stream experiments with acetylene and ethylene mixtures have clearly revealed that aging increased the selectivity of over-hydrogenation and ethylene selectivity reached negative values, i.e. ethylene present in large excess was consumed (Fig. 4). In these early studies, it was found that the catalyst preparation significantly affected aging and ethylene selectivity. Thus, it was observed [122] that in the case of supported palladium, polymeric materials are detrimental to selectivity, whereas they brought about an increase in semihydrogenation selectivity in the hydrogenation of acetylene over palladium black consisting of 50 nm particles in a spongy structure containing many large (>100 nm) pores. Using labeled acetylene and CO, it has been shown that aging by deposits results in the appearance of sites which hydrogenate ethylene to ethane even if there is sufficient amount of acetylene in the gas phase.

When located on the support, carbon deposits are confirmed to exert an undesirable effect on the selectivity of alkyne hydrogenation. In interpretation of over-hydrogenation, the effect of oligomers/deposits acting as hydrogen reservoir was cropped up. Polymeric materials migrating from the metal to the support may facilitate hydrogen surface transport to certain fraction of sites that are not covered by acetylene. Hydrogen spillover in effect increases the

availability of hydrogen, i.e. might provide a way to interpret hydrogenation of the intermediate alkene [57,122,123]. This was assumed to be the reason for the increased ethane selectivity over a Pd-on- γ -Al₂O₃ catalyst compared with Pd-on- α -Al₂O₃ [57]. The rate of ethane formation on the former catalyst is expected to be much higher due to the higher BET surface area of the γ -Al₂O₃ support. Although the effect of coke serving as hydrogenation or spillover agent is still obscure, Sermon et al. have shown that coke over silica-alumina is able to hydrogenate cyclohexene at 343 K in the presence of dissociated hydrogen available by spillover [124]. Polyaromatic compounds are proposed to be responsible for the hydrogenation activity. However, the role of polyacetylene or polyaromatics in hydrogenation of acetylene still requires a thorough study.

The variation of the product selectivity or hydrogenation of ethylene in the presence of acetylene has frequently been explained in such a way that aging generates different sites on the surface [13,31,32]. Kinetic studies by Borodziński using Pd-on- α -Al₂O₃ [76,79] and commercial catalysts [52] also led to the suggestion that the deposits formed during acetylene hydrogenation generate two types of active sites. They argued that certain sites representing small spaces of the palladium surface between carbonaceous deposits (A sites) are sterically inaccessible to ethylene. It is assumed that hydrogenation of ethylene to ethane occurs on large palladium spaces where ethylene and acetylene competitively adsorb (E sites). A simplified representation of the proposed model is given in Fig. 5. It is assumed that vinylidene species adsorbed on A sites is a key intermediate in hydrogenation of acetylene, while π -bonded ethylene adsorbed on E sites is a key intermediate in hydrogenation of ethylene. A larger steric hindrance of the adsorbed ethylene compared to that of adsorbed acetylene is

caused by the difference in position of the molecules in the adsorbed state: π -adsorbed ethylene is flat lying, whereas adsorbed acetylene as vinylidene is either perpendicular or tilted with respect to the surface.

The above interpretations do not consider the effect of transport hindrance on consecutive reactions and the effect of the accumulation of deposits on the local effective diffusivity [125]. The increase in ethane selectivity can be regarded as the consequence of increased diffusion resistance affecting the surface fugacity of acetylene inside the pores. The problem of selectivity considering pore structure and internal diffusion was already addressed by Mars and Goergels [126] and Toei et al. [127] in acetylene and in greater detail by Gaube and coworkers [128–130] in 1,3-cyclooctadiene hydrogenation.

Asplund, in his elegant studies, has shown that over Pd-on-Al₂O₃ catalysts carbon deposits substantially decrease effective diffusivity by blocking the catalyst pores [57,60]. Mass transfer limitations severely hinder intraparticle diffusion of acetylene and, consequently, an increased rate of ethylene hydrogenation in the interior of catalyst particles will result. The overall effect is decreasing alkene selectivity.

The deactivation behavior of Pd-on- α -Al₂O₃ is quite different when used in the gas- and liquid-phase hydrogenation of acetylene [60]. In the gas phase, the rate of deactivation was strongly dependent on the operating conditions and the activity and selectivity passed through a maximum (Fig. 6). In the liquid phase, catalytic activity and ethylene selectivity declined during the first part of the operation and then stabilized. The amount of oligomers was much higher in the gas-phase operation but when working at high hydrogen availability, these liquid products were easily removed. In contrast, strongly bound, highly unsaturated coke was formed in the presence of a solvent or low excess of hydrogen.

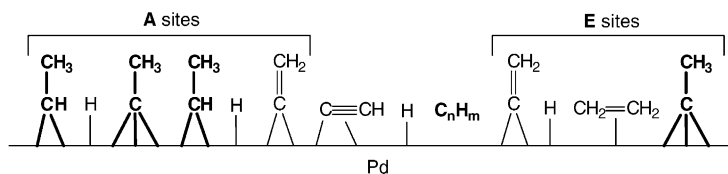


Fig. 5. The simplified representation of the palladium surface during the hydrogenation of the acetylene–ethylene mixture [52]. Irreversibly adsorbed species creating the carbonaceous overlayer are printed boldface.

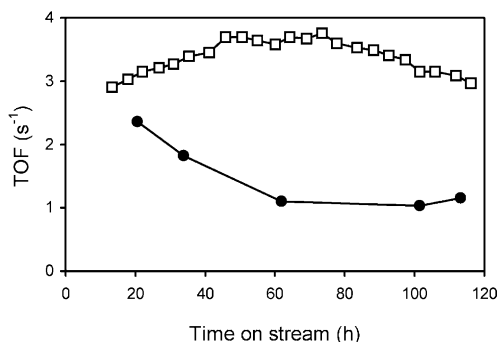


Fig. 6. Deactivation of a Pd-on- α -Al₂O₃ catalyst in the hydrogenation of acetylene in excess ethylene in the gas phase (□) and in the liquid phase (●) [60].

The amount of coke was not directly related to the increase in formation of undesired ethane in the hydrogenation of acetylene over supported catalysts [58]. Instead, the surface coverage of hydrogen during the deactivation was found to be a crucial parameter by influencing the proportion of “harmful coke” and “harmless coke”. The former type generated at low hydrogen coverage was proposed to be responsible for increased ethane selectivity by, for example, a spillover mechanism. Unfortunately, temperature-programmed oxidation analysis could not reveal evidence for the presence of the two types of coke.

Data on the fine structure of carbon deposits are rather scarce. The morphology of carbon on samples of an 0.15% Pd-on-SiO₂ industrial catalyst, developed by Degussa for the selective hydrogenation of acetylene in vinyl chloride production [131], was studied after prolonged use (from 8 months to 6 years) [53]. This catalyst shows good activity and selectivity even after long operations. Amorphous, microcrystalline and polymer-like carbon, and carbon filaments were detected on the surface. The amorphous carbon partly covered the metal, but the silica support remained partly unaffected. Fe and Cl impurities also covered by carbon suggest their involvement in carbon deposition and the shielding of Pd.

3.3. Effect of promoters on selectivity

The intrinsic ability of palladium to yield alkene selectively can be further improved by promoters (modifiers) and additives. Adding a second metal to

the catalyst either by alloying, reacting it with an organometallic precursor or in the form of metal salts may improve selectivity by altering electronic or geometric properties of palladium [87,96]. The effect of metal ions is a complex one. They may remain adsorbed in ionic form or become reduced or partially reduced by surface hydrogen depending on the relative position of the catalyst potential and the modifier metal–metal ion potential. Nevertheless, redox transformation of Pb, Sn, Ge, Bi, etc., to form adatoms on Pd or Pt or penetration of metal atoms into Pd has been convincingly demonstrated [132–135].

Changing the electron density of palladium affects the relative adsorption strength of the reactant, intermediates and hydrogen. Alternatively, the second metal may block part of the surface thereby affecting the geometry of the active site. In either way, the performance of the catalyst may be fine-tuned to yield the alkene with higher selectivity. In addition, a modifier may affect selectivity by influencing the formation of the palladium β -hydride phase.

In fact, the most selective method used traditionally by synthetic chemists for the selective semihydrogenation of acetylenes applies both a promoter and an additive. Application of the Lindlar catalyst, which is palladium deposited on CaCO₃ poisoned by lead diacetate recommended to be used in conjunction with quinoline in the reaction mixture [136], is the most selective procedure to hydrogenate alkynes to alkenes. Quinoline, which may be substituted by other amines or sulfur compounds, is supposed to compete for the active sites with the intermediate alkene. Lead, in turn, formed as a result of the reduction of adsorbed lead diacetate, changes surface properties of palladium.

Due to the practical significance, the effect of lead has been thoroughly investigated but its role in selective hydrogenation is still controversial. No specific effect other than rearrangement of the surface into larger crystallites was found in an early study [137]. Competitive hydrogenation of 2-octyne with 1-heptene indicated that a change in the metal–molecule bond strength was more decisive than mechanical blocking of the surface by lead ad-atoms [138]. The conventional Lindlar catalyst (industrial samples) and a Pd–Pb alloy supported on CaCO₃ were characterized by Palczewska et al. using XRD and XPS, hydrogen sorption and kinetic tests [139,140]. The industrial Lindlar catalyst chemisorbs hydrogen and form the

β -PdH phase, whereas the alloy catalyst only physisorbs hydrogen. The two catalysts also differ in the state of the modifying component. Lead oxide was observed on the surface of that particular Lindlar catalyst, but the alloy catalyst contained lead only in the metallic form on the surface. The alloy catalyst was found to be more selective which was attributed to the presence of a two-dimensional oligoatomic cluster of palladium atoms tailored by the localization of lead atoms in a fixed geometry existing with a stoichiometry of Pd₃Pb. The beneficial role of adsorbed lead (lead atoms bound to palladium atoms) in contrast to bulk lead (lead atoms bound to other lead atoms) was also proved by electrochemical polarization [141].

Additional studies by a variety of analytical techniques on industrial Lindlar catalysts [142], and an experimental Lindlar catalyst and lead-coated Pd foil [143] found no evidence of the formation of selectivity enhancing Pb–Pd alloy or Pb-containing surface compound. The addition of lead did not modify the electronic properties of palladium either. The selectivity increase is most likely due to morphological changes. Both studies agree that the addition of lead seems to block a selection of sites responsible for unselective hydrogenation. The increase in terrace type Pd surface atoms relative to stepped and kink sites appears to be the most likely change induced by the Lindlar treatment [143].

Alloying palladium with Group IB elements usually brings about an enhanced selectivity and increased reaction rate. Now the effects are thought to originate from the donation of electrons from these metals to palladium [144] or the variation of the ensemble size [85,145]. A different explanation was put forward in an early study where Cu was found to decrease oligomer formation [123]. Since oligomers on the support were believed to play a role in the hydrogenation of ethylene with the involvement of spilt-over hydrogen, decreased oligomer formation was beneficial on selectivity. In addition, Cu served as desorption sites for hydrogen.

In a recent detailed study using a Cu–Pd-on-pumice catalyst in the hydrogenation of phenylacetylene a decrease in activity likely due to the dilution of the palladium active sites by copper was observed [146]. The alloy catalyst, in turn, showed a better selectivity in semihydrogenation. In agreement with other studies, no change in the electronic properties of palladium

was found by the addition of copper. The increased selectivity, therefore, was attributed to the decrease in the ensemble size needed for multiple adsorbed (alkylidene) species. In another study, however, 5% Pd-on-Al₂O₃ catalysts alloyed with Ag or Au showed no change in styrene selectivity as compared to the parent Pd catalyst [147]. The beneficial effect of Ag, in turn, was observed in the hydrogenation of acetylene over a Pd–Ag-on-Al₂O₃ catalyst which was claimed to originate from the suppression of the formation of adsorbed hydrogen [148]. Bulk (adsorbed) hydrogen is assumed to result in the direct hydrogenation of acetylene to ethane (*vide supra*).

The modification of palladium catalysts with organometallic reagents has recently been pursued by reacting PbBu₄ [149–151] or GeBu₄, SbBu₄ or SnBu₄ [150] with Pd-on- α -Al₂O₃. This method is believed to create bimetallic particles. In the presence of hydrogen, all butyl groups are released and a subsequent reduction with hydrogen at elevated temperature generates the corresponding bimetallic alloys. Interaction of PbBu₄ without hydrogen with palladium atoms at the metal–support boundary was shown to produce a Bu₂Pb–Pd-on- α -Al₂O₃ precursor. In all cases with the exception of germanium, the resulting catalysts exhibited increased selectivity in the hydrogenation of 2-methyl-1-buten-3-yne [150] and acetylene in the presence of ethylene [149]. This was explained by preventing the formation of multiple adsorbed species responsible for the direct hydrogenation of acetylene to ethane due to selective blocking of the most active sites. In addition, a change in the relative adsorption strength over the bimetallic sites may also contribute to the observed effect [150]. Supportive to this suggestion is the finding that dissociative adsorption of hydrogen is suppressed [139,151]. Molecular adsorption of ethylene and the strong adsorption of acetylene were also shown to be retarded over the Pb–Pd(1 1 1) surface [139].

Amorphous PdSi and PdGe alloys also exhibited high selectivity in the hydrogenation of phenylacetylene, 1-octyne [152] and 1-hexyne [153]. The surface of Pd₈₁Si₁₉ was shown by XPS to contain metallic Pd embedded in SiO₂ matrix [153]. However, no evidence of electronic effect of the underlying amorphous material on the catalytic properties was found. Instead, the high selectivity was attributed to the properties of the palladium–silicon oxide interface. The improved

selectivity of supported Pd catalysts modified by chemical vapor deposition, in turn, was attributed to dilution of the Pd surface by Si and SiO₂. This results in suppression of the formation of ethylidyne and ethylidene species, which requires multiple adsorption sites [46]. When the SiO₂ layer is dissolved, a rough surface consisting mainly of Pd will appear which is a very active but unselective catalyst [153]. PdZr and PdCuZr alloy ribbons and powders made by rapid quenching and mechanical alloying, respectively, required pretreatments (dissolution of Zr by HF or oxidation) to exhibit activity. In contrast to PdSi, these treatments brought about increased selectivity in the hydrogenation of phenylacetylene [154].

Studies with a Pd–B-on-SiO₂ catalyst indicated remarkably high chemo- and stereo-selectivity [75]. Comparative studies with a model Pd(1 1 1)–B system indicated the geometric blockage of Pd sites by boron species leading to a decrease in the total number of active sites. This changes the ensemble size which, in turn, affects the chemisorption of hydrogen, alkyne and intermediate alkene.

A series of palladium–rare-earth-metal intermetallic compounds studied in the hydrogenation of 1-butene showed three distinct types of behavior [155]. Pd₃La easily decomposed and its surface could be considered as existing in the form of Pd-on-La₂O₃ with catalytic properties similar to those of Pd-on-pumice. Pd₃Ce was partly decomposed forming a surface of palladium sites surrounded by a catalytically active cerium compound. The high activity and low semihydrogenation selectivity of this sample was interpreted as a promotion effect of cerium on the availability of hydrogen and an electron transfer from Pd to Ce keeping palladium in an electron-deficient state. The other samples (Pd₃Sm, Pd₃Pr and Pd₃Nd), in turn, exhibited low activity and high butene selectivity, which was attributed to electron-rich palladium and weakly adsorbed hydrocarbon species.

Finally, the effect of doping a Pd-on-Al₂O₃ catalyst with potassium resulted in an increase in the probability of ethylene desorption which suggested that the strength of hydrocarbon adsorption decreased [156,157]. Furthermore, the rate of ethylene hydrogenation decreased which contrasted with an enhanced rate of acetylene hydrogenation. It was suggested that the K-doped Al₂O₃ induces an electron transfer to Pd. Pd with an increased electron density

has less propensity to share electrons with adsorbate hydrocarbons. This leads to an increase in ethylene selectivity because ethylene desorbs more readily before it can be further hydrogenated to ethane and because ethylene is less likely to readsorb and become hydrogenated. The remarkable properties of a Pd-on-pumice catalyst, namely high and stable activity, i.e. the lack of aging, and high selectivity even at high dispersion, was also attributed to the effect of alkali metal ions. A shocking thermal treatment induces the segregation of sodium and potassium from the support framework to the metal [59]. These ions decorating the metal surface, in turn, exert both geometric and electronic effects on Pd.

3.4. Effect of additives on selectivity

The synthetic method of producing alkenes by the hydrogenation of alkynes over the Lindlar catalyst is recommended to be carried out in the presence of an organic base. In his original experiments, Lindlar used quinoline [158]. Ammonia [55] or other organic bases such as piperidine [91,144] were also reported to increase alkene selectivity. The high selectivity of palladium catalysts supported on polyamides was also claimed to result from the pyridine moieties in the polymer support [73]. The general interpretation is that nucleophilic compounds are able to increase the electron density of palladium through electron donation. Increasing electron density of palladium, in turn, leads to decreasing strength of interaction with electron-rich compounds such as hydrocarbons with multiple unsaturation. The decreased strength of adsorption of the intermediate alkene would favor desorption of the alkene and increase its overall selectivity. In contrast, sulfur compounds, such as thiophene [55,159] being electron acceptors exhibit an opposite effect compacted with the effect of sulfur decreasing the content of carbon deposits on the metal.

The role of additives in selective hydrogenation of alkynes and dienes has been systematically discussed by Boitiaux et al. [159–161]. The mechanism of action of various nitrogen bases and sulfur compounds is quite complex and apparently it cannot be only explained by competition, site poisoning or the electronic/ligand effects. In a recent paper, Spencer and Yu considering the electronic effects of quinoline concentrated on the effect of the polarization of the

Pd–H bond [162,163]. It was found that in the presence of a base $\text{Pd}^{\delta+}\text{--H}^{\delta-}$ whereas in the absence (unmodified Pd-on-C) $\text{Pd}^{\delta-}\text{--H}^{\delta+}$ dominates. The effect of nitrogen bases on the preferential hydrogenation of alkynes can then be attributed to the preferred attack of the nucleophilic H on the triple bond. In general, alkenes are less reactive towards nucleophiles than alkynes. Pd treated with lead acetate behaved in a similar way and it was observed that lead increased the propensity to form $\text{H}^{\delta-}$.

In interpretation of the effect of nitrogen bases one should not disregard the fact that the modifiers can alter the surface morphology of Pd by semiextractive adsorption. One of the reasons for this phenomenon is that Pd has the lowest lattice energy of the noble metals [164]. In the Lindlar or Rosenmund reductions, significant morphological changes were observed indicating restructuring of the Pd surface caused, e.g. by treatment of Pd black in triethylamine at 423 K [137,165].

The corrosion effect of strongly adsorbing nucleophilic substrates such as vinylacetylene is well documented (below 373 K it leaches Pd from the support [161]). Fracturing and dissolution of Pd were also observed in liquid phase hydrogenation of terminal alkynes by Molnár et al. [152]. It can be noted that the catalysts were shock treated hence the amorphous structure might facilitate dissolution of Pd. Substrate induced segregation of Pd sites explains the behavior of Pd–Ag and Pd–Au in hydrogenation of phenylacetylene [147]. The catalytic activity could be well correlated with CO adsorption measurements indicating that the substrate just as CO induces segregation of Pd to the surface. Other evidences for the corrosion effect of CO are well documented [166,167]. As an additional evidence Berenblyum et al. found that Pd-on- Al_2O_3 catalysts poisoned by various sulfur compounds ($\text{C}_4\text{H}_9\text{SH}$, $\text{C}_6\text{H}_5\text{CH}_2\text{SH}$, $(\text{C}_6\text{H}_5\text{CH}_2\text{S})_2$, $(\text{C}_8\text{H}_{17}\text{S})_2$, etc.) were reactivated during hydrogenation of phenylacetylene [168].

Whereas N-containing impurities must be removed from the product stream of C2–C5 alkenes produced industrially, CO is still used in industrial applications. It is well known that small amounts of carbon monoxide have the ability to hinder hydrogenation of alkenes. This characteristic is made use of CO as feed additive in the selective hydrogenation of acetylene in the presence of excess ethylene to poison the catalyst

and thereby to avoid over-hydrogenation [169]. CO in these systems behaves as reversible poison. In acetylene streams containing large excess of hydrogen CO is commonly added in amounts near to 1000 ppm (0.1%) to keep the ethylene selectivity at the desired level. Under industrial conditions for 1% increase in CO level, the ethylene loss has been reported to decrease by 4–6%. At the same time, the acetylene ppm increases by 25% [170].

Competitive adsorption of the alkene and CO was originally suggested to interpret the beneficial effect of CO applied in the hydrogenation of alkynes. In fact, in the low temperature hydrogenation of ethylene over Pd-on-C, 0.5–2.5 ppm CO was reported to be sufficient to poison hydrogen uptake [171]. One may conclude, therefore, that in the absence of acetylene in the gas phase CO will dominate on Pd thus preventing further reactions. Palczewska et al. [139,172] has interpreted the increased selectivity of acetylene hydrogenation in such a manner that CO blocks the Pd surface for hydrogen and ethylene adsorption. CO desorption is facilitated by acetylene as shown by Cider et al. in cross-desorption studies [173–176]. Modeling hydrogenation of acetylene, ethylene and propylene at transient conditions over Pd-on- Al_2O_3 supports the view that CO plays a more important role in inhibiting ethylene hydrogenation than that of acetylene. At large acetylene pressures as shown by McGown et al. [31], the competition between CO or ethylene and acetylene is not important. Most of the studies presented recently explain the effect of CO in terms of competitive adsorption of CO with hydrogen decreasing, thereby the surface concentration of hydrogen [20,32,123]. During acetylene deuteration when CO is added, the probability of hydrogenation of adsorbed vinyl decreased which could be explained by the suppressed concentration of surface hydrogen atoms. The experiments with ethylene have shown, however, that in the presence of CO, desorption of ethylene increased allowing to conclude that displacement of ethylene by CO causes a decrease in its surface concentration [177].

The presence of CO in the acetylene feed affects the formation and composition of oligomers. Weiss et al. have observed a fast decrease in reaction rate, nevertheless, the selectivity of C4+ as a function of CO partial pressure was not much affected (Fig. 7) [123]. The selectivity of 1,3-butadiene hydrogenation increased at the expense of *n*-butenes. McGown et al. reported

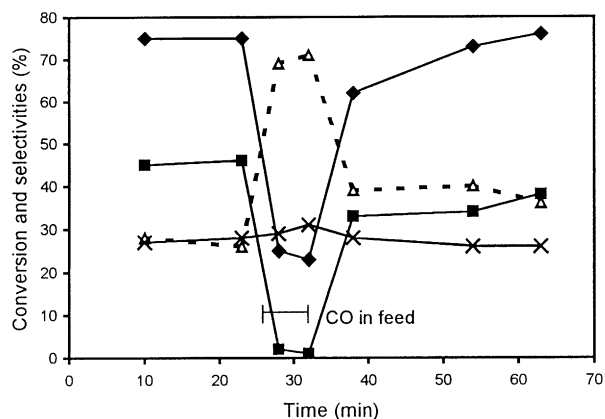


Fig. 7. Reversible effect of CO on acetylene conversion and selectivities over 0.04% Pd-on- γ -Al₂O₃ [123]. (◆) conversion, (▲) ethylene selectivity, (■) ethane selectivity, (×) C₄+ selectivity.

decreasing C₄ yield upon the increase of CO pressure [31]. Over Pd–Cu LeViness et al. found that CO decreases the selectivity of oligomer formation [34]. Surprisingly, however, CO significantly increased the carbon content of the catalysts in pilot plant studies [112].

3.5. Stereo-selectivity

Internal alkynes upon hydrogenation may yield the corresponding *cis*-alkenes with high selectivity. The preferential formation of *cis*-compounds provides further evidence for the *syn* addition of hydrogen during heterogeneous catalytic hydrogenations [10]. The *trans*-isomer is usually interpreted as being formed by the isomerization of the *cis*-compound. Since a small amount of *trans*-alkene may be formed even before the total consumption of alkyne, it is reasonable to assume that the *trans*-alkene may also be an initial product [10].

The problem of stereo-selectivity was rarely addressed in recent years and only a few papers have disclosed results on the hydrogenation of internal alkynes [72,73,75,178]. The best performance was observed with a Pd–B-on-SiO₂ catalyst which showed 96.7% selectivity at 99.99% conversion of 2-butyne [75]. A 99.9% selectivity in the hydrogenation of 12-tetrahydropyranyloxy-3-tetradecyne at the same degree of conversion is even more remarkable.

Moreover, the same high selectivity was maintained after the disappearance of the starting alkyne. These properties were accounted for by a change in the ensemble size induced by boron adspecies. In contrast, selectivities obtained on palladium supported on polyamides are rather low which are obviously due to the high isomerizing activity [73].

The polymerization of (EtO)₃SiH in water by Pd(OAc)₂ yields finely divided palladium dispersed in a polysiloxane matrix [178]. This catalyst is able to hydrogenate alkynes in the presence of (EtO)₃SiH as the hydrogen source to yield *Z*-alkenes with better than 96% stereo-selectivity.

4. Hydrogenation of dienes

4.1. Conjugated dienes

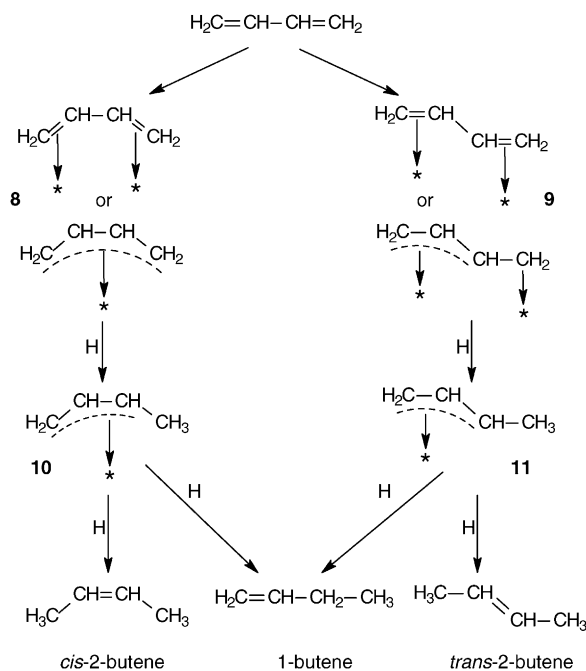
The regioselective hydrogenation of a diene is essentially governed by the same effects that determine the relative reactivities of monoalkenes during competitive hydrogenation in binary mixtures: a terminal double bond exhibits higher reactivity than other, more substituted double bonds and, therefore, it is hydrogenated preferentially [10]. A different kind of selectivity also arises when a diene is hydrogenated, since the newly formed monoene and the unreacted diene compete for the same active site. The reactivity of conjugated dienes, in general, exceeds that of monoenes and even nonconjugated dienes. This is attributed to the fact that the entire π -system of dienes is involved in adsorption through di- π -coordination, which is more favored than the di- σ mode of adsorption of a single double bond [24].

Due to its practical importance and theoretical significance, the semihydrogenation of 1,3-butadiene was still extensively studied in the last decade [179–200]. Furthermore, data are also available for isoprene [150,201,202], 1,3-cyclooctadiene [203–209] and other conjugated dienes [73,138,210–212].

A whole range of various supported palladium specimens including Pd-on-Al₂O₃ [179,182–184,198, 200–202], Pd-on-SiO₂ [179,194,202,207], Pd-on-pumice [192,205–207], Pd deposited on C [185,194, 202,212] or graphite [185,194,199], Pd-on-Nb₂O₅ [210], Pd-on-CaCO₃ [202], Pd-on-BaSO₄ [202], Pd-on-ZnO [195], Pd-CeO₂-Al₂O₃ [196], Pd black

[202], and Pd on polymeric supports [73] was used as catalyst. Bimetallic palladium samples [138,150,180,186,189–192,203,204,209], mainly with Group IB metals [181,183,187,188,193,197,202,203,211,213] were also the subject of studies to learn the effect of the second metal on the catalytic properties being selectivity the high concern.

Monohydrogenation of 1,3-butadiene can take place by either 1,2 or 1,4 addition to produce 1-butene or 2-butenes, respectively. It was early established that, in contrast with other Group VIII metals, and copper and gold, formation of 1-butene and *trans*-2-butene (with only a small amount of *cis*-2-butene) is characteristic of palladium [214]. In addition, isomerization of alkenes formed is suppressed in the presence of the diene. The proposed reaction intermediates and reaction routes suggested by Wells et al. [215,216] are shown in Scheme 5. The *trans*:*cis* ratio in the range of 8–12 indicates that interconversion between the conformers of 1,3-butadiene and that of the surface adsorbed species **8** and **9** are limited. The *trans*-isomer, consequently, is formed from the dominant, more stable *S-trans* conformer through 1,4 addition with the involvement of π -allyl intermediate **11**. The *S-cis*

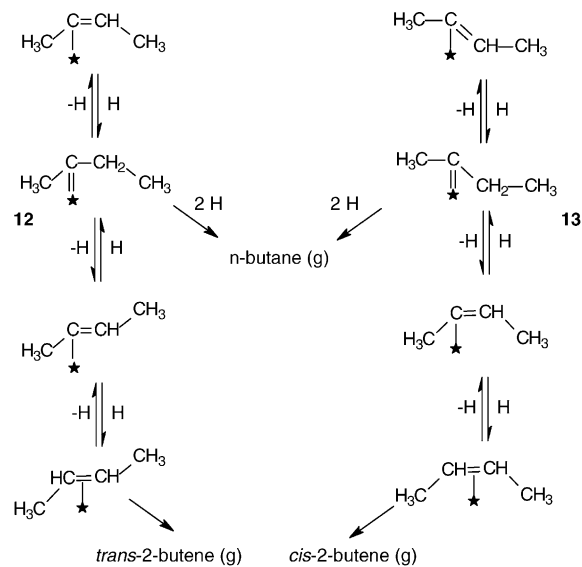


conformer, in turn, gives π -allyl intermediate **10** and ultimately yields *cis*-2-butene. Product selectivities in the hydrogenation of isoprene (distribution of the three methylbutene isomers) provided further evidence for the involvement of π -allyl intermediates [202,217].

In recent years, Boitiaux et al. have proposed a novel interpretation [218]. Their mechanism assumes that conformational interconversion of diene species is slow on all metals in comparison to hydrogenation and the adsorbed diene mimics the concentrations of *S-trans*- and *S-cis*-1,3-butadiene in the gas phase. Their mechanism includes formation of carbene species (**12** and **13**) to explain the formation of *n*-butane as a direct product of 1,3-butadiene hydrogenation and the comparable *cis*- and *trans*-selectivity for 2-butenes over Group VIII metals. This part of the mechanism is shown in Scheme 6. According to this scheme, metals, which do not promote formation of intermediate carbene, e.g. Pd, neither allow high conformational interconversion between *trans* and *cis*-species, nor hydrogenate directly to *n*-butane.

4.1.1. Effect of dispersion on activity and selectivity

Although fewer data are available for dienes than for alkynes, the correlation between the activity of palladium catalysts and dispersion in the hydrogenation of dienes is more straightforward: a strong



antipathetic behavior is usually found [185,194,199, 200,202,205–207,219]. Sometimes the specific activity is constant up to a certain dispersion value (20–35%) depending on the support [205,207,219] but then decreases with increasing palladium dispersion. The strong structure sensitivity observed in the hydrogenation of conjugated dienes was interpreted by invoking the peculiar electronic structure of small palladium particles. The electron-rich diene strongly chemisorbs on these small, electron deficient clusters as compared to large particles leading in effect to self-poisoning [90,202,219]. It is of interest to note that over carbon support the activity decreased only in the 3–1.5 nm range. An upward shift in the Pd 3d core level energy as compared to the values for massive Pd particles [194,199], ionization loss spectroscopy (ILS) [185,194] and the diminution of the density of states near the Fermi level [199] seem to support the conclusion that a change in the electronic properties (intrinsic initial state effect) is responsible for the activity loss on the small particles.

The decrease in activity was shown to largely depend on the pressure of hydrogen and the diene over Pd vapor-deposited on graphite [199]. With low diene partial pressure and in the presence of large excess of hydrogen the activity of the smaller Pd aggregates was comparable to that of larger particles. The phenomenon was attributed to a size dependent deactivation due to carbon deposits which, in turn, was related to a change in the electronic properties. A different explanation was put forward for low-loaded Pd-on- α -Al₂O₃ catalysts [200]. Reaction rate, chemisorption, TEM and XPS data [44] show that different metal particle morphologies exist depending on the way of preparation. Strong interaction of Pd with the support results in the formation of small, flat Pd particles (rafts) rendering the particles less active. It was proposed that on these particles (1 1 1) faces appear in high propensity [220,221].

In fact, sites of threefold symmetry on (1 1 1) favor multiple bonding and apparently they exhibit very low value for hydrogen sticking probability. Hydrogenation of 1,3-butadiene has been documented to be face sensitive over Pd [222] and Pt [223]. Over both metals, the activity increases in the order (1 1 1) < (1 0 0) < (1 1 0).

Pumice-supported palladium catalysts, again, show similar unique characteristics observed for the

hydrogenation of alkynes [205–207]. They are resistant to oxidation, the turnover frequency in the hydrogenation of 1,3-cyclooctadiene is maintained even at high metal dispersion [207] and their activity is always higher than those of other supported catalysts. In addition, the selectivity is very high (100% up to complete conversion of the diene) [205,207]. The selectivity ratio expressed as the ratio of the rates of the consecutive hydrogenation steps (k_1/k_2) is always very high (above 700) with a maximum around 35–45% dispersion. These features were explained by the presence of alkali metal ions (Na⁺ and K⁺) on the surface of the support. The ions donate electrons to palladium which results in a weaker interaction with the electron-rich substrate. A negative shift, i.e. a decrease in the binding energy in the Pd 3d core level energy in the Pd-on-pumice catalysts testifies to the increased electron density [205,207].

4.1.2. Effect of carbon deposits

In gas phase hydrogenations rapid self-poisoning of diene hydrogenation was observed especially at low H₂:diene ratios both in flow [193] and in static circulation systems [182,183]. Stable activity could only be obtained after many hours time on stream or after repeated restart experiments. During the initial period, the Pd sites become gradually covered with surface species which remain on the sites. FT-IR investigations on adsorption of C₄ hydrocarbons point to formation of both “end attached” (butylidyne, 3-butenylidyne) and “flat lying” (di- σ , quad- σ , di- σ/π , etc.) adsorbed species [224]. Detailed studies over Pt single crystals do also report large carbon coverages equivalent to one diene per two or three Pt atoms [223].

Peculiar observations were made in studying the hydrogenation of 1,3-butadiene over a catalyst prepared from an amorphous Pd₂Ni₅₀Nb₄₈ ribbon [186,190]. Activation of the amorphous sample resulted in the formation of a Pd–Ni-on-Nb₂O₅ catalyst which showed high semihydrogenation selectivity (Fig. 8). Over the just activated sample the rates of diene and 1-butene hydrogenation and that of 1-butene isomerization were commensurable. However, on the self-poisoned surface hydrogenation and isomerization of butenes were remarkably inhibited, nevertheless, the catalyst remained active in the hydrogenation of 1,3-butadiene. It was proposed that the unusually high alkene selectivity after depletion of butadiene

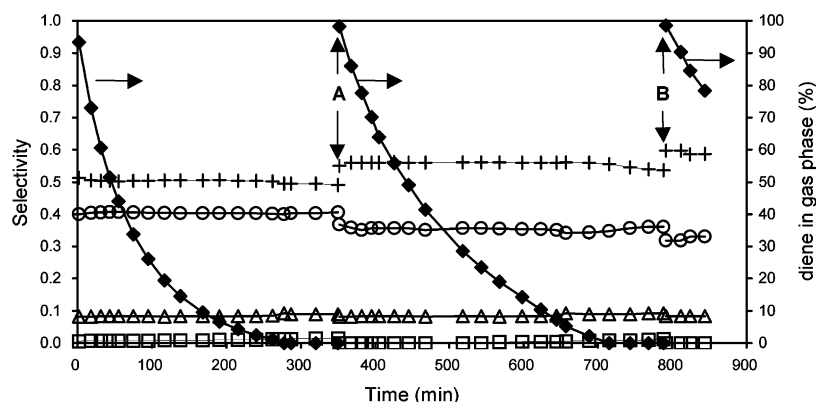


Fig. 8. Hydrogenation of 1,3-butadiene over $\text{Pd}_2\text{Ni}_{50}\text{Nb}_{48}$. Initial H_2 :diene ratio = 3.4. Arrows A and B indicate restart experiments ((\square) *n*-butane, (+) 1-butene, (\circ) *trans*-2-butene, (\triangle) *cis*-2-butene) [190].

was ensured by firmly held adspecies formed from the diene. Apparently, adsorption of butenes is hindered by these adspecies whereas 1,3-butadiene, through its strong complexation strength, compresses firmly held adspecies layer thereby creating reaction sites for its semihydrogenation. The adsorbed hydrocarbon overlayer in that particular case behaves as a filter due to its intermediate strength of adsorption between diene and alkene. Similar aging features were observed at Pd–Ni samples prepared by vapor phase deposition of $\text{Pd}(\text{acac})_2$ and $\text{Ni}(\text{CO})_4$ and then submitted to calcination, reduction and partial deactivation by hydrogenation of 1,3-butadiene [225]. Hydrogenation treatment only ensured low activity since the samples without oxygen treatment were contaminated by carbon. These deposits acted, however, as non-selective poison. Self-poisoning of the activated sample in time-on-stream experiments ensured, however, the high selectivity of *n*-butenes formation in hydrogenation of 1,3-butadiene and 1-butene mixtures.

Gas phase hydrogenation studies due to the rapid carbon poisoning allow also the investigation of the selectivity behavior under high C–Pd coverages ($\text{mg deposit/g}_{\text{cat}}$). Detailed studies by Sárkány with eggshell type catalysts with low palladium content (0.05% Pd-on- α - Al_2O_3 , 0.04% Pd-on- γ - Al_2O_3) showed that accumulation of surface hydrocarbons decreases catalytic activity in the hydrogenation of 1,3-butadiene and facilitates butane formation [182,183]. The ratios of 1-butene:2-butenes and *trans*-2-butene:*cis*-2-butene also decreased. A part of the

surface carbon may dissolve in the bulk to form PdC_x ($x < 0.15$) whereas the larger part of the carbonaceous deposits is sitting on both metal and support sites. The hydrocarbon film formed over the surface results in transport hindrance, i.e. a decrease in the effective diffusivity. Diene concentration over the working catalyst sites, consequently, is low and, therefore, intermediate butenes are not displaced immediately by diene molecules. The longer residence time of butenes increases the chance for complete hydrogenation and also explains the observed low values for the isomeric ratios. The crucial factor in keeping high butene selectivity, therefore, is to prevent formation and accumulation of oligomers and deposits in the shell. In a similar way, hydrocarbonaceous deposits turned an originally highly selective Pd–Ag-on- α - Al_2O_3 catalyst into a non-selective one by decreasing diene transport rate [187,197]. As a result, the effective surface concentration of the diene decreases and the displacement of butenes by diene becomes slower than hydrogen addition to butenes.

In a comparative study on the behavior of uniform and eggshell Pd-on- δ - Al_2O_3 catalysts in the hydrogenation of 1,3-butadiene, the former showed much higher deactivation rate [201]. The quantity of coke accumulated was also higher and this coke had higher molecular weight. In contrast, the coke formed over the eggshell type catalyst composed of mainly aromatic compounds. These may easily diffuse out from the catalyst pore mouth hindering the formation of high molecular weight coke. The latter may cause

diffusion hindrance and pore plugging resulting in decreasing butene selectivity.

4.1.3. Results with bimetallic catalysts

Industrial palladium catalysts applied to remove diene impurities from olefin feedstocks tend to give rise to undesirable side-reactions namely the hydrogenation and isomerization of the desired alkene. These transformations can be minimized by using bimetallic catalysts.

Most of the observations acquired in the hydrogenation of dienes over bimetallic catalysts indicate that addition of a second metal to palladium results in a decrease in catalytic activity and an increase in semihydrogenation selectivity [87,96]. This was observed in the hydrogenation of 1,3-butadiene over palladium catalysts alloyed with Group IB metals (Pd–Ag-on- α -Al₂O₃ [181], eggshell type Pd–Ag and Pd–Au supported on Al₂O₃ [213], and Pd–Ag-on-SiO₂ [192]). A Pd–Cu-on-Al₂O₃ catalyst (Pd:Cu = 5) selectively hydrogenates virtually all (>99%) of the 1,3-butadiene to butenes without significant isomerization or over-hydrogenation [193]. This high effectiveness was accounted for by the suppressed hydrogen sorption, both the surface adsorption and the bulk absorption (hydride formation). As a result, the availability of atomic hydrogen for surface reaction diminishes which creates a more stable surface environment for the direct hydrogenation of 1,3-butadiene to butenes.

The above pattern, i.e. decreasing activity and increasing selectivity, was also observed for Pd–Cr-on-SiO₂ [191]. Decreasing activity was attributed to dilution effect caused by Cr or oligomerization induced by chromium oxide covering the surface [191]. Electronic effects leading to a favorable change in the adsorption constant of 1,3-butadiene with respect to that of butenes was invoked to explain the high (100%) selectivity. In contrast, both the activity and the selectivity were diminishing when 1,3-cyclooctadiene was hydrogenated over a Pd–Pt-on-pumice catalyst [204]. This could be expected since Pt is known to be less active and less selective than Pd in the hydrogenation of highly unsaturated hydrocarbons. In addition, the Pt–diene bond is much stronger than the Pd–diene one and, therefore, the intermediates formed are more stable increasing the possibility for complete hydrogenation to the alkane. Pt allows hydrogenation of

both diene and alkene due to the smaller difference in the free energy of adsorption than over Pd. In turn, polymer-protected Pd–Pt bimetallic cluster catalysts containing at least 50 at.% Pd showed higher activity than a typical colloidal palladium catalyst [209]. Selectivity of the formation of cyclooctene was almost 100% with Pd content above 60 at.%. It was shown that bimetallic clusters with a composition of Pd:Pt = 4 have a platinum core surrounded by Pd atoms. Since Pd atoms are selectively located on the surface the cluster catalysts exhibit selectivities similar to those of pure Pd colloids.

A rather unique example is the behavior of Pd-on-ZnO [195]. When treated with hydrogen at temperatures above 423 K, the ZnO support undergoes partial reduction to form Pd–Zn intermetallic phases. Zn metal decorates Pd sites which significantly decreases the available Pd sites and, consequently, suppresses catalytic activity. The suppression of complete saturation to form butane is in accordance with the very limited hydrogen chemisorption capacity of these samples.

In other cases, bimetallic catalysts exhibited higher activity than the corresponding monometallic Pd sample. Such behavior is rather surprising for Pd–Ag and Pd–Au supported on SiO₂ in the hydrogenation of isoprene with insignificant changes in selectivity [202]. Progressive isolation of palladium atoms with increasing Au or Ag content and, therefore, a change in the electronic structure of palladium was invoked for explaining the observations. The activity of Pd₅₀Cu₅₀ single crystals was also higher in the hydrogenation of 1,3-butadiene [188]. Again, changes in the electronic properties of palladium and the resulting changes in the chemisorptive properties of the reactant and intermediates may be responsible for the phenomenon observed. The diene hydrogenation activity was also investigated over Cu(1 1 0) surface modified by Pd. Pd in the monolayer and submonolayer range was inactive [226]. At about three monolayers, the activity reached a maximum which is higher than over Pd(1 1 0) by a factor of 8. The activity increase has been attributed to stress effects, which create special sites by distorting locally the atomic bonds.

Colloidal Pd–Cu clusters with Pd:Cu ratios higher than unity exhibited the same activity as the pure Pd sample [203]. The polymer-protected (poly(*N*-vinyl-2-pyrrolidone)) bimetallic powders

exhibited extremely high selectivity. It was suggested that the polymer works as a position-blocking ligand, whereas Cu acts as an electron-releasing ligand influencing the coordination ability of the reacting 1,3-cyclooctadiene.

Pd₁Ni₉₉ and Pd₅Ni₉₅ alloys used in the hydrogenation of 1,3-butadiene were shown to undergo surface palladium enrichment (20 and 50 at.% Pd on the surface, respectively) exhibiting the same activities as Pd(111) or Pd(110) [180]. The observed changes were proposed to be associated with two effects. A diluting effect results in the formation of active sites composed of small groups of Pd atoms or Pd pairs. These pairs are then electronically modified by the surrounding Ni atoms. The surface and catalytic properties of Pd–Ni has been further tested over Pd–Ni-on-SiO₂ [227,228], (111)- and (110)-oriented Pd₈Ni₉₂ single crystals [229], Pd–Ni(111) [230,231] and Pd–Ni(110) surfaces [232,233] prepared by deposition of Pd.

Pd deposited on Ni(111) caused only a small increase in the activity without any selectivity changes in comparison to Pd(111). Over Ni(110) faces, Pd deposited in four monolayers greatly enhanced the activity (Fig. 9). The large difference in the atomic size causes surface strain that induces the formation of superstructures resulting in Pd sites of specific geometric arrangement [232–234].

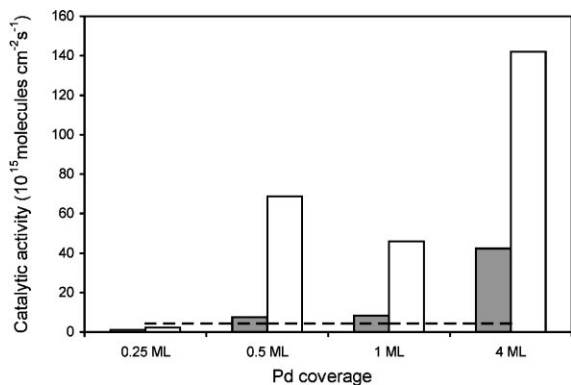


Fig. 9. Catalytic activity for the hydrogenation of 1,3-butadiene on Pd–Ni(110) as a function of monolayer coverage of Pd ($p_{\text{H}_2} = 20$ Torr, H:diene = 5, $T = 295$ K). Dark bars: without annealing; white bars: after annealing at 475 K; broken line: activity of Pd(110)) [232,233].

Pd₃Ce and Pd₃Zr intermetallic compounds were shown to exhibit greater selectivity for butene formation than a Pd sponge especially at high 1,3-butadiene conversions (0.9 versus <0.7 at 100% conversion) [235]. It was demonstrated that these samples have a surface layer consisting of Pd in a rare-earth oxide matrix. It is suggested that strong metal–support interactions may affect the electronic structure of Pd leading to the superior selectivity of these catalysts.

Finally, observations with Pd–rare-earth catalysts [155], bimetallic palladium catalysts prepared from organometallic precursors [150], and Pd–Pb [138] applied in the hydrogenation of conjugated dienes are essentially the same found for alkynes already discussed in Section 3.3.

4.1.4. Effect of additives

The influence of additives on competitive hydrogenation of dienes and alkenes and the factors affecting intrinsic selectivities can be interpreted in a similar way as in alkyne hydrogenations.

Furukawa, in a series of papers, reported the effects of various additives on the liquid phase hydrogenation of industrial C₄ fraction containing 1,3-butadiene [236,237]. Addition of CO to the feed decreased the hydrogenation rate and practically eliminated 1-butene isomerization. CO behaved as reversible poison and a CO:H₂ ratio of about 4 was claimed to give the best results. The effects of presulfiding with H₂S were also tested. They observed that 100 ppm of H₂S were sufficient for butadiene removal down to 20 ppm with little butene loss. Pd catalyst over-sulfided could be regenerated by hydrogenation of diene and alkene mixtures. The catalyst in the presence of 100 ppm H₂S showed good long-run stability concerning activity and selectivity. Addition of other inorganic compounds, such as Cl₂, COCl₂, N₂O, N₂O₃ and SO₂, has also exerted a positive effect on reaction selectivities.

Hydrogenation of 1,3-butadiene over presulfided Pd-on-Al₂O₃ facilitates sulfur removal. In line with the observation of Furukawa et al., Oudar reported displacement of preadsorbed sulfur during 1,3-butadiene adsorption and hydrogenation over Pt(110) [238]. In the presence of diene overlayer, the Pt–S binding energy decreased by 15–22%. Using AFM and XPS it was found that sulfur adsorption on Pd catalysts not only reduces the number of active sites but also weakens the adsorption strength of remaining sites [239].

It was clear that the addition of sulfur compounds affected the surface morphology of Pd. In the presence of H₂S, Monzón et al. observed a significant decrease in *n*-butenes selectivity [240]. In spite of this, initial small extent of poisoning appeared to be beneficial as sulfur deactivated mainly sites responsible for overhydrogenation.

4.2. Nonconjugated dienes

Since nonconjugated dienes do not play any crucial role in large-scale industrial processes, only few studies are available for their selective hydrogenation. Nevertheless, the hydrogenation of 1,5-hexadiene is of interest as a model reaction for the hydrogenation of the undesirable C10–C14 alkadienes to alkenes utilized in the production of linear alkylbenzenes to synthesize biodegradable detergents.

Pd-on-Al₂O₃ shows high activity and good global selectivity (percentage of diene converted to hexenes) but the fractional selectivity is low: it produces *trans*-2-hexene as the main product instead of the desired 1-hexene [211]. This is attributed to the high activity of palladium to induce double bond migration and form 2,4-hexadiene as an intermediate which, then, undergoes hydrogenation to yield 2-hexenes. When niobia is used as the support fractional selectivity is greater than 50% at low conversions [210]. These catalysts show the usual structure sensitivity, i.e. decreasing selectivity with increasing dispersion as observed in the hydrogenation of alkynes and conjugated dienes. Hydrogenation of 1,5-hexadiene in excess 1-hexene (89.5 mol%) over Pd-on-Al₂O₃ shows rather low selectivity for *n*-hexenes. This is the consequence of the fact that isolated dienes behave like alkenes and there is no significant difference between adsorption coefficients as indicated by the rather fast isomerization of 1-hexene [241]. Nevertheless, using TiO₂ support and increasing its acidity with WO₃ the alkene selectivity was observed to increase. The improved *n*-hexene selectivity could be correlated with the isomerization activity of the catalyst to produce 1,4- and 2,4-hexadienes.

The change in activity and selectivity by adding a second metal followed the usual pattern already discussed. Pd–Ag-on-Al₂O₃ catalysts with Pd:Ag ratio of about unity were much less active than the monometallic sample [211]. All bimetallic catalysts showed good

global selectivity and improved fractional selectivity. The best catalyst, in terms of 1-hexene yield, is 7.1 wt.% Pd–1.8 wt.% Ag-on-Al₂O₃. Dilution of Pd by Ag atoms is suggested to hinder the ability of palladium to promote isomerization (double bond migration) since this reaction requires multiple sites. The observations and conclusions with Pd–Sn-on- γ -Al₂O₃ catalysts containing surface Pd₃Sn and Pd₂Sn species are exactly the same as with the Pd–Ag bimetallic samples [242,243]. The selectivity to *n*-hexenes was 91–92% at 90% conversion of 1,5-hexadiene and the 1-hexene selectivity over 5.17 wt.% Pd–0.77 wt.% Sn (Sn:Pd atomic ratio = 0.13) reached 45% [243].

Competitive hydrogenation of 1,7-octadiene with alkenes allowed to draw the same conclusion as for similar studies with alkynes and alkenes [28,29] (Section 2, Table 1).

5. Membrane catalysis

There is continuous interest in using palladium membranes in the hydrogenation of alkynes and dienes. The membrane may be palladium itself or it may serve as support for the catalytic species. In the latter case, inorganic membranes (e.g. porous alumina) or thin organic polymer films are used. The catalytic reaction is most often carried out in the permeation mode allowing hydrogen to diffuse through the membrane to the reactant. Alternatively, hydrogen is mixed with the reactant and the mixture is allowed to contact with the membrane (premix mode). In most cases, palladium membranes are more selective than the corresponding non-membrane catalysts. This is due to the lower hydrogen pressure allowing to suppress side-reactions and to shifting the steady-state concentration of reactants and products away from the equilibrium over the working catalyst.

In his pioneering work, Gryaznov applied bimetallic dense palladium membranes [244,245]. When a Pd–Ru membrane was used a yield of 98% was reported in the hydrogenation of the triple bond of dehydrolinalool to produce linalool a valuable intermediate in the production of fragrances [246]. Selectivities with other bi- and tri-metallic membrane catalysts (e.g. Pd–Pb, Pd–Mn) were above 95% [247,248]. Cyclopentadiene was hydrogenated with 92% selectivity [244].

A Pd/ γ -Al₂O₃ membrane supported on α -Al₂O₃ was tested in the hydrogenation of acetylene and 1,3-butadiene [249]. The highest selectivity to the partially hydrogenated products occurred when the reactants were premixed with hydrogen. For the acetylene reaction, an excess of hydrogen was required (H₂:C₂H₂ = 8, 200°C), whereas a high selectivity to butenes was observed with a stoichiometric amount of hydrogen at 30°C. Increased selectivities obtained with the membrane catalyst as compared to those determined with a conventional Pd-on- γ -Al₂O₃ catalyst were attributed to a decrease in contact time between the reactants and hydrogen.

Xu and coworkers have reported the use of polymeric hollow fiber reactors in the hydrogenation of cyclopentadiene [250–252], isoprene [251], 1,3-butadiene [251,253], and propadiene and propyne [254]. The membrane catalysts were prepared by pumping an aqueous solution of PdCl₂ in polyvinylpyrrolidone (PVP), melamine-formaldehyde resin or ethyl cellulose through hollow fibers of cellulose acetate (CA), polysulfone or polyacrylonitrile (PAN) then reducing the palladium salt by hydrazine or NaBH₄. All membrane catalyst were active and stable under mild conditions (40°C, 0.1 MPa). PVP-Pd/CA and PVP-Pd/PAN exhibited better than 91% conversion and selectivity in the hydrogenation of conjugated dienes [251]. Propene selectivity was 97.8% when propadiene and propyne impurities in propene were hydrogenated [254]. Permeation mode experiments always gave better results [250,253]. Pd, Pd₉₃Ni₇, Pd₉₃Ru₇, and Pd₇₇Ag₂₃ membranes also showed better performance in the permeation mode when used in the hydrogenation of acetylene [255].

A remarkable synergic effect was observed when 1,3-butadiene (0.6%) was hydrogenated in crude 1-butene [253]. PVP-Pd/CA was found to be the best catalysts, but 2.6% 2-butene was detected in the product. The isomerization of 1-butene, however, was completely suppressed over a PVP-Pd-Co/CA bimetallic membrane catalyst. This catalyst also showed excellent characteristics in the selective hydrogenation of cyclopentadiene [252].

Despite some attractive features and substantial efforts for improvements, commercial utilization of membrane catalysis by palladium is limited by the difficulties of membrane fabrication and engineering, heat and mass transfer problems, low surface area,

and the issue of hydride formation resulting in embrittlement and, eventually, mechanical deterioration and cracking.

6. Industrial applications

In the previous sections, the unique catalytic behavior of Pd in semihydrogenation of multiple carbon–carbon bonds has been demonstrated. Apparently, Pd has high activity in activation of molecular hydrogen and, in the presence of stream additives or catalyst modifiers, provides extremely high chemo-selectivity in competitive hydrogenation of acetylene or diene in olefins. This almost magic property makes Pd a very attractive catalyst in many industrial applications, since after removal of acetylene and diene impurities to ppm levels, the hydrogen treated alkene stream is the feedstock of several downstream applications.

C₂–C₅ alkenes are mainly produced by steam cracking (SC) and catalytic cracking (CC) and only smaller amounts are obtained from catalytic dehydrogenation, viscosity breaking, fluid coking, ethylene/butene metathesis, methanol-to-olefins processes, oxidative dehydrogenation or dehydration of alcohols, etc.

Steam cracking of C₂–C₃ alkanes, LPG and naphtha is a pyrolysis process operating at 1073–1173 K in the presence of steam and was invented to produce large quantity ethene for respective downstream applications [1,256–258]. In Europe and the Far East, the preferred feedstock is naphtha, whereas saturated hydrocarbons (ethane, propane and LPG) is used mainly in the Middle East countries and USA. Naphtha or gas oil pyrolysis, due to the rather unselective nature of thermal processes, leads to different alkenes, cycloalkenes, aromatics and highly unsaturated hydrocarbons such as dienes and alkynes.

Significant amounts of light alkenes are produced by CC in refineries from vacuum distillates, deasphalted oil or partly pretreated resids and used in downstream processes to produce octane boosters [259–263]. About 40% of propene is already produced by FCC and the demand is growing continuously. C₄ and C₅ alkene cuts are mostly used for production of alkylate (reaction of isobutane and alkene) or MTBE and TAME which have gained significant

importance as a source of oxygen in the gasoline blend. The active constituent in modern FCC catalysts is an ultra stabilized zeolite Y (USY) which is rear earth exchanged to maintain high silica:alumina ratio and large pore size to fulfill the requirements of FCC unit and to maximize branched HC production. Addition of medium pore size ZSM5 additive (1–3 wt.%) increases production of isobutylene and isopentene yields [262]. Deep catalytic cracking (DCC), owing to more severe conditions, produces more light olefins than FCC units and DCC can be operated in modes which produce maximum propylene or maximum isoolefins.

Catalytic dehydrogenation depending on season and location may be attractive in production of alkenes such as propene or isobutylene. Houdry CATOFIN (ABB Lummus Crest Inc.) works at low pressures (less than atmosphere) at about 873–923 K [264]. Snamprogetti FBD operates in fluid bed allowing a simple transfer of the aged catalyst into regeneration section [265]. Both processes use chromia-alumina catalyst. Pt based catalysts are utilized in Oleflex (UOP) and STAR (Steam Active Reforming, Phillips) processes operating at 873–900 K [266,267].

The alkene streams produced by thermal processes mentioned above are inevitably contaminated by acetylene and diene impurities. These highly unsaturated molecules, due to their strong complexation and high reactivity, cause problems in respective applications. Dienes and acetylenes poison the Ziegler–Natta polymerization catalyst. Like most of the organometallic compounds they are sensitive for highly unsaturated contaminants. It is not surprising, therefore, that the regulations are extremely strict for the allowed level of multiple unsaturated hydrocarbons, metals (As, Hg, Si, etc.), CO, COS and O₂ impurities in chemical and polymerization grade alkenes [169,268,269]. Metallocene single site catalysts are even more sensitive and the concentration of multiple unsaturated compounds must be <1 ppm.

In alkylation reactions, the presence of multiple unsaturated increases the acid consumption especially in the older H₂SO₄ based processes. Increasing the severity of CC to improve RON (which is required for heavier crude oils) also increases the diene concentration in the C4 stream sent to alkylation unit. The H₂SO₄ based alkylation technology is very sensitive for diene impurities: each kilogram butadiene

consumes about 13 kg of sulfuric acid [270], causing problems in the recovery of acid or elimination of the acidic resin (150–200 kg acid/t alkylate). HF units are less sensitive for dienes; acid consumption is typically 80–100 kg acid/t alkylate.

The raw alkene mix produced in the steamcracker oven is quenched, compressed, washed, dried and cooled. The produced mix is then separated into C₂, C₃, C₄ and C₅+ streams. Selective semihydrogenation of dienes and acetylenes in alkene streams over Pd (or Ni) catalyst is the only economic process for obtaining high purity polymerization grade alkene streams. Catalytic hydrorefining has been proven to be a reliable way of upgrading alkene streams. Extraction, distillation or extractive distillation processes are not selective enough at ppm level. Moreover, the catalytic processes not only remove the troublesome acetylene and diene impurities but also transform them to valuable olefins increasing thereby the overall yields. Several catalytic hydrogenation processes are devoted for steamcracker downstream treatments. An excellent review has already been compiled by Derrien [169]. In this paper, we present a few new processes introduced in the past years.

6.1. Selective C₂ hydrotreatment

The hydrogenation converter, acetylene-removing unit (ARU), follows the rectification line and is integrated in the low temperature section of the ethylene plant. The C₂ fraction can be taken [256] from either the deethanizer overhead (tail-end hydrogenation, Fig. 10) or from the compression train of the cracked gas at one of the compressor interstage levels before H₂, CH₄, CO and C₃+ were removed (front-end hydrogenation, Fig. 10). In the front-end mix, the C₂ stream contains high percentage of methane and hydrogen. CO formed by water gas shift reaction in the pyrolysis tubes ($C + H_2O = CO + H_2$) decreasing thereby the amount of the carbonaceous deposits is inevitably present. CO, as discussed in Section 3.4, is a reversible poison which decreases the activity while increases the overall ethene selectivity. Its fluctuation causes problems in the uniform operation of ARU. In addition, CO incorporates into the oligomers resulting in the formation of various carbonyl compounds (aldehydes and carboxylic acids) increasing thereby the average molecular weight.

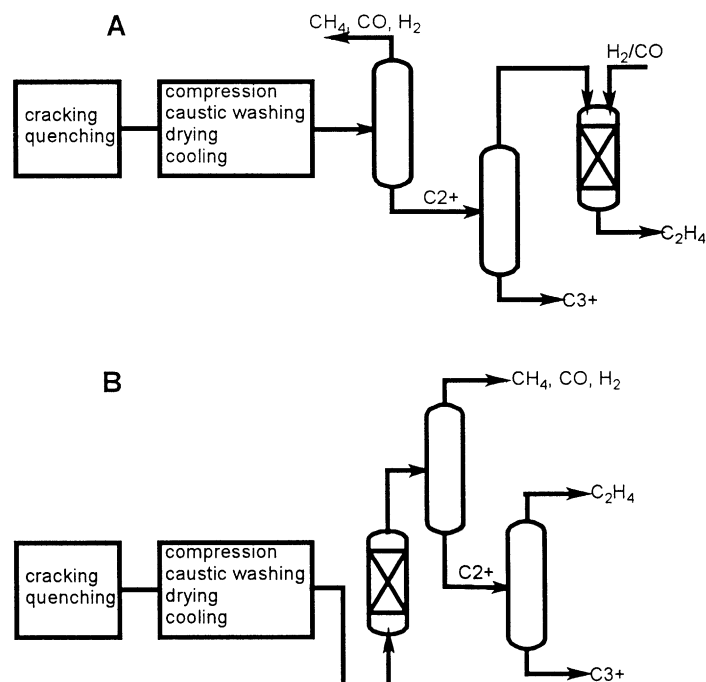


Fig. 10. Simplified process flow of tail-end (A) and front-end (B) hydrogenations of acetylene.

It is a convenient way of acetylene removal to treat the overhead of ethylene–ethane fractionator. In the tail-end cuts taken from deethanizer top, the ethylene:acetylene ratio is typically 50–200 and the acetylene is present in 0.5–2% v/v (5000–20 000 ppm). The H_2 :acetylene ratio ranges from 1.2 to 2.2. The operation is performed in the gas phase at 15–30 bar with space velocity between 1000 and 3000 $\text{m}^3/\text{m}^3 \text{ h}$ [271,272]. Depending on the acetylene concentration, hydrogenation is performed in cooled tubular reactor or one or two adiabatic reactors. The heat generated is removed by intercooling between the reactors in the latter case. The activity of the fresh regenerated catalyst is regulated by CO. The CO concentration is gradually decreased as oligomer/polymers build up on the catalyst bed and the catalytic sites become poisoned. As a consequence of self-poisoning, the catalyst bed temperature should then be increased, reaching 393 K at the end of the cycle, to maintain conversion of acetylene.

The overall selectivity of ethene largely depends on the catalyst applied. The trend for these converters is

to use small amount of CO (1–3 ppm) or operate the reactor without CO.

Front-end hydrogenation of acetylene requires early separation of C_4 's to preserve butadiene. The conditions of operation are similar to those used in tail-end hydrogenation. Hydrogenation is performed in tubular or bed reactors with two or three separate beds to allow heat removal and careful control of the temperature along the bed. The Pd catalysts (0.01–0.05 wt.% Pd) are designed to meet the strict requirements: high selectivity for ethylene yield, excellent stability and high flexibility in feedstock qualities. In front-end hydrogenation CO is a necessary feed additive due to the high percentage of hydrogen. Bimetallic promoted catalysts have been proved to provide better ethene selectivity than monometallic ones. The second component such as Ag [273,274] increases the temperature gap between clean up temperature and run away temperature. The former is the temperature required for a given level of acetylene, the latter one represents the temperature at which the ethene selectivity is still positive. KataLeuna offers Pd–Cu

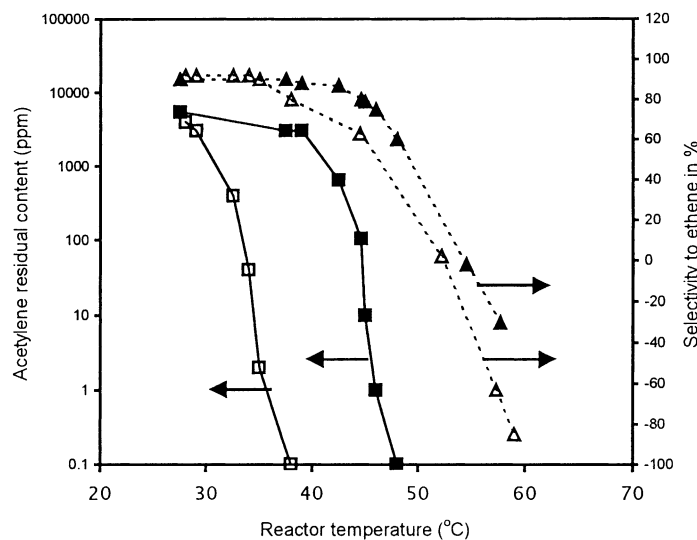


Fig. 11. Influence of CO concentration and temperature on acetylene ($H_2:C_2H_2 = 35$) over Leuna catalysts 7741 (promoted Pd on alumina). Open symbols: in the presence of 212 ppm of CO; shaded symbols: in the presence of 849 ppm of CO (from [275] with permission by the authors).

based catalysts, 7741 and 7741R for front-end-cut and 7741A and 7741A/R for tail-end-cut [275]. Typical results obtained in front-end hydrogenation are shown in Fig. 11. The support material is stabilized alumina of low surface area. Another important requirement is to produce as little amount of oligomers as possible. Oligomers/polymers decrease the catalytic activity, increase the selectivity of over-hydrogenation (ethane formation), cause flooding in reactor tubes and foul heat exchangers. The acid sites of the support are proposed to participate in oligomer formation. SiO_2 offers the lowest acidity and in recent times using based on SiO_2 BASF introduced H O-11 and H O-20 promoted Pd catalysts [271,272].

In order to avoid or at least to diminish some of the problems caused by formation and accumulation of oligomers/polymers, IFP (Institut Francais du Petrole) introduced the so-called solvent recirculation Acetex process [276]. A simplified process flow is presented in Fig. 12. The recirculating solvent removes continuously the oligomers from the catalyst bed, thereby decreases the probability of formation of heavy oligomers and carbonaceous deposits. The heat capacity of the solvent phase increases the thermal stability of the reactor and prevents formation of hot spots. In the presence of solvent phase, acetylene is

removed only to a certain limiting value and a second reactor operating in the gas phase is added to reach ppm level of acetylene.

In the C3 fraction, the impurities removed by semi-hydrogenation are methylacetylene (MA) and propadiene (PD). Depending on the severity of pyrolysis, the concentration of MAPD is 1–4% v/v. The MAPD concentration in propene produced by FCC is significantly lower (ca. 0.01%), but the C3 stream may contain other impurities such as AsH_3 which due to similar boiling points appears in C3. Hydrogenation of MAPD can be performed both in the gas phase and the liquid phase. The C3+ cuts are received in liquid form and it is convenient, therefore, to perform the hydrogenation in trickle bed (Bayer process) [277–280] or mixed phase (IFP process) [281] rather than to evaporate, chill and compress the C3 stream again.

6.2. C4 fraction hydrorefining

After-hydrogenation treatment of crude C4 cuts is a complex process due to the large number of constituents and possible downstream applications. C4 fraction produced by pyrolysis of butane or naphtha contains 0.1–1.2 wt.% vinyl-acetylene, 35–70 wt.% butadiene, 1–15 wt.% 1-butene, 3–6 wt.%

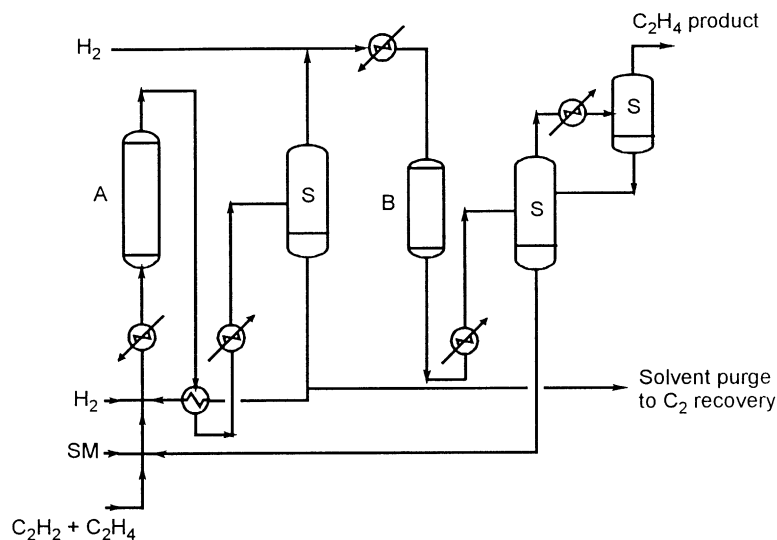


Fig. 12. IFP Acetex process. A: mixed phase reactor; B: vapor phase reactor; S: separator; SM: solvent makeup.

trans-2-butene, 2–4 wt.% *cis*-2-butene, 20–28 wt.% isobutylene, 0.5–5 wt.% isobutane and 1–25 wt.% *n*-butane. In processing the C4 cuts, the following hydrogenation treatments are applied.

1. Hydrogenation of vinylacetylene in butadiene-rich fraction. This process is part of the diene extraction process and the objective is to optimize diene recovery. The low hydrogenation temperature used frequently in the liquid phase operations causes problems because vinylacetylene extracts Pd from the catalyst surface. This problem is usually avoided by performing the operation above 373 K. Procatalyse developed LD 277: the promoter added helps to stabilize the Pd phase. In addition, Cu [282–284], PdBi₃/Al₂O₃ [285] and PdTe₄/Al₂O₃ [285] are good candidates for vinylacetylene hydrogenations. The latter two catalysts allow hydrogenation at 303–313 K at 5–6 bar pressure.
2. Hydrogenation of diene-rich fraction selectively to *n*-butenes. At present there is diene surplus in Europe [286,287] and this tendency is likely to continue. Semihydrogenation of diene adds a certain flexibility to react on the market requirements and improves the profitability of the whole process. Among numerous technologies, we mention only Hüls SH-CB (selective

hydrogenation-concentrated butadiene) [287–289] or BASF Selop C4 (selectivity optimized) processes [290,291].

3. After diene extraction and diene semihydrogenation (Raffinate I) and isobutylene removal, the *n*-butene-rich fraction (Raffinate II) contains 0.5–2.5 wt.% butadiene which must be selectively removed to 50 ppm, and in some cases <10 ppm. C4 fraction rich in 1-butene is a valuable comonomer for production of LLDPE (linear low density polyethylene). To ensure low diene remaining concentration and to keep high 1-butene selectivity, special care is required in catalyst formulation and process conditions. The Hüls process prevents 1-butene transformation to 2-butenes by dissolving CO in C4. IFP introduced promoted bimetallic catalyst (Procatalyse LD 271) for the same purpose [144,270,292]. BASF Selop C4 process can be optimized to get high yield of 1-butene or 2-butenes by changing the operation parameters [290,291].
4. Hydroisomerization process is applied to transform 1-butene to 2-butenes. In alkylation reaction higher RON can be obtained with 2-butenes than with 1-butene. Isomerization of 1-butene to 2-butenes also facilitates separation of isobutylene and 1-butene which, due to very similar boiling points,

cannot be rectified economically by distillation. Pd being a highly active catalyst for double bond shift is applied in these processes (see, for example, Arco-Engelhard (HPN IV-B) [293–296], Phillips Hydroisom [297] or IFP processes [298]). The reaction is performed in hydrogen at about 373 K due to the low rate of isomerization in comparison to hydrogen addition. LD 265 developed by Procatalyse ensures full removal of diene, 100% *n*-butenes selectivity and 2-butene:1-butene ratio >12 [299].

5. In addition to selective diene hydrogenation, full hydrogenation of diene to *n*-butane may be an opportunity to eliminate surplus diene (e.g. Hüls CSP (complete saturation process) [287,289]). The least valuable *n*-butane is usually returned to the pyrolysis oven. Direct steamcracking of Raffinate I would result in the loss of highly valuable isobutylene, moreover, diene would cause considerable carbon deposition on the pyrolysis tubes.

Hydrogenations above are performed in the liquid phase. The prototype of these hydrogenation technologies is the Bayer Cold Hydrogenation process operating in trickle phase. Semihydrogenation is achieved in a series of adiabatic trickle-bed reactors and the heat evolved is removed by recycle cooling. The crucial parameter in these processes is the mass or pressure regulation of hydrogen close to the stoichiometric amount. It requires a careful design of these reactors to control the local temperatures in the presence of excess hydrogen. To avoid formation of “hot-spots” uniform wetting of the catalyst particles and uniform gas–liquid distribution over the catalyst zones are required for mixed phase systems. Over-hydrogenation and the run away were avoided in Hüls SHP process by dissolving the stoichiometric amount of hydrogen in the hydrocarbon feed. At low diene content, hydrogenation is also performed isothermally, i.e. the more expensive shell side cooled tubular reactor is applied with pressure regulation of the cooling system. The operating pressure in adiabatic operation is defined in such a way that the liquid phase operation at each temperature (function of diene content and activity of the catalyst) should be ensured. One of the great advantages of liquid (or mixed) phase operations that oligomerization/polymerization occurs to far lesser extent than in gas phase operation because the C4 phase (solvent) removes these materials from the catalyst surface.

6.3. Hydrotreatment of C5+ cuts

C5+ fraction or pyrolysis gasoline in naphtha crackers consists of C4 column residue and the so-called quench oil. The raw hydrocarbon mix is highly unstable due to the large concentration of diolefins (10–15 wt.%) which give not only unpleasant smell but they are also the source of polymer gum formation. Stabilization of the gasoline boiling range fraction by semihydrogenation yields high-octane gasoline blending (RON is between 95 and 103 depending on the severity of cracking). C6–C8 aromatics fraction can be recovered that after hydrogen treatment (C5+ contains 60–85 wt.% aromatics) provides high purity aromatics. Hydrogenation of gasoline is generally performed in two stages. The objective of the first stage hydrogenation is to stabilize the C5+ fraction which means selective hydrogenation of diolefins (pentadiene and isoprene) and cycloolefins, and alkenylaromatics into the corresponding olefins and alkylbenzenes, respectively. BASF SELOP C5+ hydrogenation process treats gasoline over Pd H O-22 containing 0.25 wt.% Pd on high surface area alumina. The Bayer and IFP processes do also apply Pd catalysts. In the first stage, hydrogenation of Pd is again the preferred metal due to its high activity allowing low temperature operation and sufficient resistance against feedstock impurities. Procatalyse offers LD 265 Pd based catalyst in addition to Ni based catalysts (LD 241, LD 155 and LD 145). The hydrocarbon stream from the first stage selective hydrogenation unit is usually sent to depentanizer. The C6–C8 fraction from deoctanizer is the feedstock of the second stage hydrogenation. The second stage hydrogenation is aimed at removing all the monoolefins and sulfur. The C6–C8 fraction is then sent for solvent extraction to yield high purity aromatics. The second stage hydrogenation performed over Ni-Mo, Co-Mo catalysts ensures alkene and sulfur removal in the gas phase.

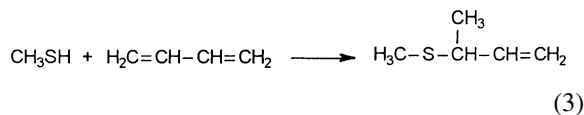
The C5+ is not only a valuable component of gasoline blend but after the first stage hydrogenation treatment, at least recent applications show in that direction, is a source of different valuable hydrocarbons whose fractionation enhances the economy of C5+ downstream treatment. Thus, at BASF C5 cut treatment, the pretreated C5 is selectively hydrogenated to remove cyclopentene and then the C5 stream is etherified with methanol to produce TAME.

Full hydrogenation of C5 produces useful solvent for polymer industry.

FCC C4 and C5 cuts present a serious challenge to the hydrogenation catalyst due to the presence of 20–400 wt.% ppm S. The usual solution is removal of mercaptans by treatments with caustic. Nevertheless, a cheaper alternative solution is the application of Pd, Ni or sulfur resistant bimetallic catalysts. Procatalyse offers LD 2773 catalyst containing promoted Pd resistant to COS for this purpose. The catalyst shows moderate isomerization activity providing a better feedstock for sulfuric acid alkylation process.

The CD Hydro process [300,301] developed over the years was invented for treatment of both FCC and steamcracker cuts. CD Hydro unifies rectification and catalytic hydrogenation in a single operation unit (Fig. 13). The selective hydrogenation catalyst (Pd or Ni) is placed at the top of the distillation tower and hydrogen is added together with the hydrocarbon stream. Excess hydrogen is removed through a vent on the top of the reflux drum. The unit operates at pressures lower than the conventional fixed bed reactors and, therefore, compression of hydrogen is normally not required. Another significant difference is that the constant pressure boiling system ensures an essentially isothermal operation as opposed to adiabatic fixed bed reactors. The catalyst bed consists of

three zones. In the bottom zone over Pd or Ni catalysts, mercaptans react with diolefins and form stable thioethers (e.g. Eq. (3)).



The high boiling points of these compounds allow easy separation from C4 or C5 alkenes. The second zone hydrogenates acetylene and remaining dienes. The continuous removal of oligomers with reflux free of acetylene and diene prevents polymer deposition and thereby prolongs the lifetime of the bed. The third zone is essentially a finishing zone which participates in double bond shift and regulates the *cis:trans* ratio. The capital cost savings seem to be substantial (50–80%). It can be noted, however, that distillation requires good vapor–liquid contact, therefore, a packing with large void fraction is required, which may be a problem in these applications with catalyst bed inside. Moreover, one must find catalysts and conditions of operation where deactivation of the catalyst bed and thus the number of regeneration cycles can be minimized.

Production of high alkene yields requires both process optimization and very careful optimization

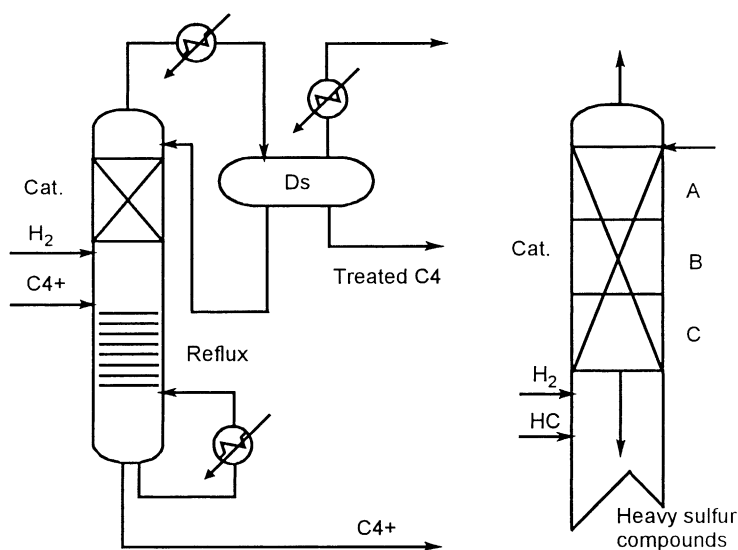


Fig. 13. CD Hydro process. A: isomerization; B: selective hydrogenation; C: desulfurization; Ds: drumseparator.

of the inherent catalytic properties. Bimetallic catalysts allow larger degree of freedom to tune the activity and selectivity to optimum performance [145,273,274,302]. In Sections 3.1 and 4.1.1, we have shown that high metal (Pd) dispersion is disadvantageous in semihydrogenation. In the case of bimetallic catalysts, such as Pd-Ag, Pd-Au, the “broken bond model” [303,304] predicts segregation of the second component which, in the case of small clusters, will occupy corners and edges preferentially and, therefore, these low coordination sites cannot participate in diene–acetylene complexation. The industrial catalysts are carefully assembled not only in the nanometer scale but also in the micrometer one. Alumina or silica support free of acid sites is impregnated in such a way that the active component appears only on the surface of the support pellets. In order to get high alkene selectivity rather narrow eggshell profiles are necessary. Choosing the right impregnation profile for both Pd and the promoter metal the hydrogenation activity moving inside the pellet can be deeply suppressed even in the 0.03 mm eggshell profile [305]. It is also an important requirement that high transport rates should be ensured [128–130,305], therefore, the Pd particles must be located in macropores. The decrease in transport rates caused by liquid oligomers or plugging of pores enhances over-hydrogenation. Since catalyst fouling by deposits is a crucial problem in these operations, further efforts are required to diminish oligomer/polymer formation. Bimetallic catalysts drastically reduce self-poisoning ensuring thereby increased cycle length of the operation and longer lifetime of the catalyst.

7. Other applications

In addition to large scale downstream applications such as hydrogenation of acetylene and diene impurities in alkene streams Pd based catalytic hydrogenations are frequently used in preparation of fine and specialty chemicals. Pd as shown in previous chapters is highly selective in forming *cis*-alkenes when disubstituted carbon–carbon triple bonds are hydrogenated.

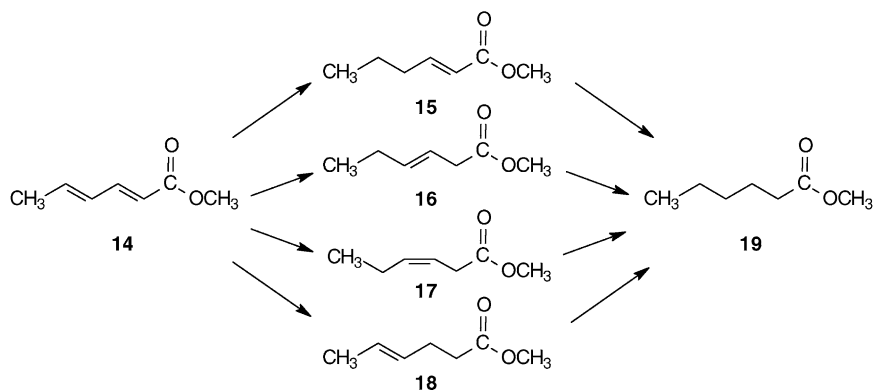
The acetylene function can easily be built into molecules by coupling terminal acetylenes with organic halides and then in a catalytic step the alkyne is converted to the corresponding *cis*-olefin. This quite

common synthesis strategy is useful for the preparation of chemical substances of high value such as food additives (Vitamins A and K), scent and fragrant substances [306], monomers (1,4-butanediol, 1,4-cyclooctadiene), sex pheromons [307], prostaglandins [308], etc. Hydrogenation of conjugated aliphatic dienes generally produces a mixture of isomeric alkenes and the selectivity of isomers depends on the starting substrate. Hydrogenation of alkynols and dienols to the corresponding unsaturated alcohols, which are important components in many applications, is also of interest. In the following only a few relevant examples are presented.

Sorbic acid synthesized from ketene and crotonaldehyde is an important selective growth inhibitor for certain bacteria. Catalytic or chemical reduction of *trans,trans*-2,4-hexadienic acid produces the corresponding hexen-1-ols which are important components of fruit odors and flavors [306,309–312]. Methyl *trans*-2-hexenoate has a characteristic odor used in numerous flavor compositions. The reaction route of methyl sorbate (**14**) hydrogenation is shown in Scheme 7 [312].

Hydrogen addition to the C(4)–C(5) double bond yields methyl *trans*-2-hexenoate (**15**) as the main reaction product. Stereoisomeric methyl 3-hexenoates (**16** and **17**) and methyl *trans*-4-hexenoate (**18**) are formed as side intermediates. Further hydrogenation of all intermediates gives methyl hexanoate (**19**). Investigations by Červený et al. [310–312] have shown that Pd-on-C exhibits high activity in these liquid phase hydrogenations and the selectivity of methyl *trans*-2-hexenoate reached 74% at 94.2% conversion of the initial substance. Formation of this compound was almost three times faster than the sum of the formations of the other isomers.

Leaf alcohols (*cis*-3-hexen-1-ol and *trans*-2-hexen-1-ol) are valuable components of fruit and vegetable fragrances and flavors. They are produced in an amount of 400 tons per year [313], via the *cis*-selective partial hydrogenation of the corresponding hexyn-1-ols. Selective formation of *cis*-3-hexen-1-ol can be ensured by using optimized Lindlar-type catalysts. Bönnemann et al. [314] have recently tested various Pd colloids on various supports in the hydrogenation of 3-hexyn-1-ol. In preparation of the catalysts, the surfactant applied does not only protect the nanoparticles but acts as a catalyst modifier. They



Scheme 7.

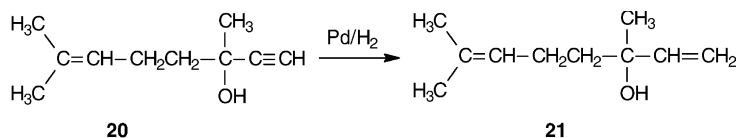
have observed that the stabilization of Pd colloids by a zwitterionic surfactant, e.g. sulfobetaine (SB12), increased the *cis*-selectivity in comparison with cationic tetraalkylammonium surfactants. Pb addition further enhanced the *cis*-selectivity: over the catalyst promoted by 2 wt.% Pb, both the selectivity and the activity were better than those over a traditional Lindlar catalyst. Surprisingly, Pd-on-C was shown to be less selective than Raney Ni in the production of leaf alcohols from *trans,trans*-2,4-hexadienol [212].

Linalool (3,7-dimethylocta-1,6-diene-3-ol, **21**) produced in an amount of 6000 tons per year is [313] a fragrant substance of the terpenic series used in several scent compositions and cosmetic preparations. In its synthesis, dehydrolinalool (3,7-dimethyloct-6-en-1-yne-3-ol, **20**) is selectively hydrogenated over Pd to the corresponding diene (Scheme 8). The acetate of dehydrolinalool can be converted to citral, another perfume intermediate. Dehydrolinalool is also an intermediate in the synthesis of β -carotene (provitamin A) developed by BASF and can be produced by reacting $\text{NaC}\equiv\text{CH}$ with methylheptenone a key intermediate in terpene chemistry.

In the selective semihydrogenation of dehydrolinalool, the catalyst composition and its form are of

crucial importance. Gryaznov et al. [247] has prepared clusters of Pd, Pd–Mn and Pd–Pb inside the pores of stainless steel metal sheet and tested the catalysts in liquid phase hydrogenations. The selectivity to linalool over Pd clusters was, however, only 80%. The presence of Pb or Mn has improved the selectivity to some extent reaching 95 and 96%, respectively, over bimetallic clusters. BASF has applied vapor phase deposition of Pd and Bi on stainless steel support to prepare a hydrogenation catalyst for the conversion of dehydrolinalool [315]. They obtained linalool with 99.3–99.5% selectivity at 100% conversion.

A Pd-containing polymer, derived from polystyrene–polybutadiene triblock copolymers and bis(acetonitrile) palladium chloride deposited on Al_2O_3 , provided a selectivity of 98.7% [316]. More recently, a novel catalyst preparation of Pd colloids has been reported by Sulman et al. [317]. The Pd colloids were formed in cores of block copolymer micelles derived from polystyrene–poly(4-vinylpyridine). The micelle cores play the role of nanoreactors providing stabilization and size control. The highest selectivity of linalool (99.8%) was observed in toluene under hydrogen-diffusion-limited conditions. The high selectivity can also be attributed to geometric–electronic



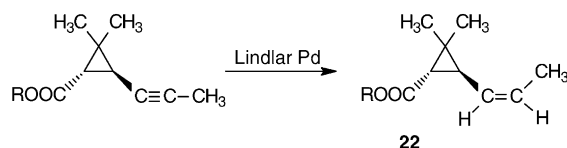
Scheme 8.

modification of Pd particles caused by the presence of 4-vinylpyridine units just as observed previously (see previous chapters) in the application of various promoters in semihydrogenations (N-bases, pyridine, quinoline, etc.) over Pd/Al₂O₃.

Pheromones are sex attractants which play a crucial role in finding the female by the male insects and thus facilitate reproduction. Obviously, the males can also be desinformed, so they remain isolated. Most of these components contain isomers of unsaturated straight chain aliphatic alcohols, acetates or aldehydes and the stereoisomeric composition is a crucial factor in their biological effectiveness [307]. One of the possibilities to get C14, C16 or C18 monoene alcohols or acetates is to hydrogenate selectively over Pd, the carbon–carbon triple bond in the corresponding acetylenic precursors to produce the *cis*-stereoisomers. Hydrogenation of enynols to the corresponding dienols provides a way to prepare conjugated dienes via acetylenic routes. Lindlar-type catalyst or Pd-on-BaSO₄ modified by quinoline are frequently used in the catalytic semihydrogenation. Palczewska et al. [318] in preparing Pd–Pb alloy catalysts have found that catalysts containing mainly Pd₃Pb intermetallic compound show higher stereo-selectivity in the semihydrogenation of 11-hexadecynyl acetate and 12-tetrahydropyranyloxy-3-tetradecyne than a commercial Lindlar catalyst.

Butane-1,4-diol is a monomer of high importance in polymer chemistry [319]. One of the many possibilities for its preparation is hydrogenation of butyne-1,4-diol over Ni. The nickel-catalyzed hydrogenation is typically a one-stage process producing the saturated diol and side products. Recent applications tend to apply two-stage processes: Pd–Ag-on-Al₂O₃ [320] or Pd modified by Pb or Zn [321] are used for selective preparation of but-2-ene-1,4-diol which is then further hydrogenated over Ni. The two-stage process provides the end-product with less impurities and higher selectivity can be achieved than applying Ni based one-stage processes.

Partial hydrogenation of natural oils [322–324] to various edible products is a large-scale process performed over Ni catalysts (supported or Raney Ni) as the best compromise on cost, selectivity, number of recycling, etc. The objective in hydrogenation of triglycerides is to reduce the level of trienic fatty acids, keep the selectivity of *cis*-isomers while not



Scheme 9.

producing saturated chains. The olefinic bonds in fatty acids found in natural oils are not conjugated but it is assumed that more reactive conjugated dienes are formed over the catalyst as the double bonds migrate up or down the chain. The conditions of operation are basically determined by the origin of natural oils, i.e. by the plants. With Ni catalysts, the temperatures applied are between 400 and 470 K and the pressure is up to 4 bar. Pd is more active but, unfortunately, more sensitive and more expensive than Ni. Nevertheless, there are indications that Pd might be applied industrially in these processes as indicated in a recent review by Savchenko and Makaryan [325].

Finally, the last example refers to pyrethrins (**22**) which are active insecticidal constituents of pyrethrum (chrysanthemum) flowers. The most prominent are pyrethrin-I and pyrethrin-II. In contrast to phosphate esters pyrethrins are not harmful to warm-blooded animals. The final crucial step in the production of the semisynthetic derivative pyrethroids is the formation of the *cis*-propenyl side chain applying the Lindlar catalyst (Scheme 9) [326].

8. Conclusion

As a result of extensive studies, the basic factors controlling selectivities in the semihydrogenation over heterogeneous palladium catalysts of alkynes and dienes were established by the 1980s. This knowledge served as the basis of industrial processes to remove hydrocarbon impurities with multiple unsaturation from alkene feedstocks. State-of-the-art Pd catalysts developed for industrial applications are capable of removing acetylene/diene impurities to ppm level without loss of alkene.

The last decade has seen a burgeoning of literature data providing further insight into the fine details of these selective hydrogenation processes. Most importantly, the application of sophisticated surface science

techniques permits to treat selectivity as a dynamic process. It has become widely accepted that the catalytic sites are generated upon the exposure of the reactant acetylene/diene and that the state of the working catalyst surface is quite different from an initially clean surface as a consequence of poisoning and restructuring effects. According to recent observations, the surface of the working catalyst is covered by an array of carbon deposits affected by reaction conditions (temperature, reactant ratio) and catalyst characteristics (dispersion, the quality of support). Promoters further modify the surface and affect the electronic properties of palladium. Additives interfere with the adsorption of reactants and may also influence the formation of surface residues. This new set of information acquired recently enables us to have a better control of the overall process and further improve selectivities by an appropriate choice of catalysts, promoters and additives and fine tuning reaction conditions. In a similar fashion, the combination of new emerging experimental techniques providing in situ on line characterization of the working sites and the traditional approach, trial and error methods will certainly promise further developments in coming years. Future trends require the most efficient use of alkene cuts in downstream applications. Large fraction of these small alkenes will be produced by FCC operation supplying cheap but highly contaminated alkenes. Development of catalysts ensuring environmentally clean operation and exhibiting high poisoning resistance towards various impurities requires further studies on appropriate manipulation and nanometer scale assembling of Pd sites.

Acknowledgements

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References

- [1] L. Kniel, O. Winter, K. Stark, *Ethylene: Keystone to the Petrochemical Industry*, Marcel Dekker, New York, 1980.
- [2] W. Weirauch, *Hydrocarbon Process.* 77 (9) (1998) 25.
- [3] P.E. Bagget, *Petroleum Technol. Quart.* (1998) 7.
- [4] S. Zehnder, *Hydrocarbon Process.* 77 (2) (1998) 59.
- [5] R.A. van Santen, P.W.N.M. van Leeuwen, J.A. Moulijn, B.A. Averill, *Stud. Surf. Sci. Catal.* 123 (1999) 64.
- [6] P.N. Rylander, *Catalytic Hydrogenation over Platinum Metals*, Academic Press, New York, 1967 (Chapters 4 and 5).
- [7] P.N. Rylander, *Catalytic Hydrogenation in Organic Syntheses*, Academic Press, New York, 1979 (Chapters 2 and 3).
- [8] P.N. Rylander, *Hydrogenation Methods*, Academic Press, London, 1985 (Chapters 2 and 3).
- [9] H. Pines, *The Chemistry of Catalytic Hydrocarbon Conversions*, Academic Press, New York, 1981 (Chapter 3).
- [10] M. Bartók, J. Czombos, K. Felföldi, L. Gera, Gy. Göndös, Á. Molnár, F. Notheisz, Pálincó, Gy. Wittmann, Á. Zsigmond, *Stereochemistry of Heterogeneous Metal Catalysis*, Wiley, Chichester, 1985 (Chapters 3 and 4).
- [11] E.N. Marvell, T. Li, *Synthesis* (1973) 457.
- [12] V. Jäger, H.G. Viehe, *Methoden der Organischen Chemie (Houben-Weyl)*, Vol. 5/2a, 1977, Thieme, Stuttgart, p. 687.
- [13] G. Webb, in: C. Kemball, D.A. Dowden (Senior Reporters), *Catalysis*, Vol. 2, The Chemical Society, Burlington House, London, 1978, p. 145.
- [14] D. Parker, in: F.R. Hartley (Ed.), *The Chemistry of Functional Groups. The Chemistry of the Metal–Carbon Bond*, Vol. 4, Wiley, Chichester, 1987 (Chapter 11).
- [15] S. Siegel, in: B.M. Trost, I. Fleming (Eds.), *Comprehensive Organic Synthesis*, Vol. 8: Reduction, Pergamon Press, Oxford, 1991, p. 417.
- [16] R.L. Augustine, *Heterogeneous. Catalysis for the Synthetic Chemist*, Marcel Dekker, New York, 1996 (Chapters 15 and 16).
- [17] M. Bartók, Á. Molnár, in: S. Patai (Ed.), *The Chemistry of Functional Groups. Supplement A3: The Chemistry of Double-Bonded Functional Groups*, Wiley, Chichester, 1997, p. 867.
- [18] H. Arnold, F. Döbert, J. Gaube, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, VCH, Weinheim, 1997, p. 2165.
- [19] G.V. Smith, F. Notheisz, *Heterogeneous Catalysis in Organic Chemistry*, Academic Press, San Diego, 1999 (Chapter 2).
- [20] A.N.R. Bos, K.R. Westerterp, *Chem. Eng. Process.* 32 (1993) 1.
- [21] G.C. Bond, D.A. Dowden, N. Mackenzie, *Trans. Faraday Soc.* 54 (1958) 1537.
- [22] T. Ouchaib, J. Massardier, A. Renouprez, *J. Catal.* 119 (1989) 517.
- [23] X.-C. Guo, R.J. Madix, *J. Catal.* 155 (1995) 336.
- [24] P. Sautet, J.-F. Paul, *Catal. Lett.* 9 (1991) 245.
- [25] A. Renouprez, NATO ASI Ser., Ser. C, *Metal-Ligand Interactions*, Vol. 378, 1992, p. 125.
- [26] L. Červený, *Catal. Rev.-Sci. Eng.* 24 (1982) 503.
- [27] L. Červený, *Chem. Eng. Commun.* 83 (1989) 31.
- [28] Z. Dobrovolná, L. Červený, *Collect. Czech. Chem. Commun.* 62 (1997) 1497.
- [29] Z. Dobrovolná, P. Kačer, L. Červený, *J. Mol. Catal. A: Chem.* 130 (1998) 279.
- [30] W.T. Tysoe, G.L. Nyberg, R.M. Lambert, *J. Chem. Soc., Chem. Commun.* (1983) 623.

- [31] W.T. McGown, C. Kemball, D.A. Whan, *J. Catal.* 51 (1978) 173.
- [32] A.S. Al-Ammar, G. Webb, *J. Chem. Soc., Faraday Trans. 1* 75 (1979) 1900.
- [33] J. Margitfalvi, L. Guzzi, A.H. Weiss, *React. Kinet. Catal. Lett.* 15 (1980) 475.
- [34] S. LeViness, V. Nair, A.H. Weiss, Z. Schay, L. Guzzi, *J. Mol. Catal.* 25 (1984) 131.
- [35] H. Molero, B.F. Bartlett, W.T. Tysoe, *J. Catal.* 181 (1999) 49.
- [36] W.T. Tysoe, G.L. Nyberg, R.M. Lambert, *Surf. Sci.* 135 (1983) 128.
- [37] L.L. Kesmodel, G.D. Waddill, J.A. Gates, *Surf. Sci.* 138 (1984) 464.
- [38] T.P. Beebe Jr., J.T. Yates Jr., *J. Am. Chem. Soc.* 108 (1986) 663.
- [39] H. Hoffmann, F. Zaera, R.M. Ormerod, R.M. Lambert, J.M. Yao, D.K. Saldin, L.P. Wang, D.W. Bennett, W.T. Tysoe, *Surf. Sci.* 268 (1992) 1.
- [40] A. Sandell, A. Beutler, A. Jaworowski, M. Wiklund, K. Heister, R. Nyholm, J.N. Andersen, *Surf. Sci.* 415 (1998) 411.
- [41] T.G. Rucker, M.A. Logan, T.M. Gentle, E.L. Muetterties, G.A. Somorjai, *J. Phys. Chem.* 90 (1986) 2703.
- [42] R.M. Ormerod, R.M. Lambert, *J. Chem. Soc., Chem. Commun.* (1990) 1421.
- [43] R.M. Ormerod, R.M. Lambert, *Catal. Lett.* 6 (1990) 121.
- [44] J. Goetz, M.A. Volpe, A.M. Sica, C.E. Gigola, R. Touroude, *J. Catal.* 153 (1995) 86.
- [45] S.D. Jackson, G.J. Kelly, *Curr. Top. Catal.* 1 (1997) 47.
- [46] E.W. Shin, C.H. Choi, K.S. Chang, Y.H. Na, S.H. Moon, *Catal. Today* 44 (1998) 137.
- [47] Ph. Maetz, R. Touroude, *Appl. Catal. A* 149 (1997) 189.
- [48] D. Tessier, A. Rakai, F. Bozon-Verduraz, *Bull. Soc. Chim. Fr.* 133 (1996) 637.
- [49] S.D. Jackson, N.J. Casey, *J. Chem. Soc., Faraday Trans.* 91 (1995) 3269.
- [50] D. Duca, F. Frusteri, A. Parmaliana, G. Deganello, *Appl. Catal. A* 146 (1996) 269.
- [51] T. Kitamura, M. Sugeta, G. Sakata, *Stud. Surf. Sci. Catal.* 121 (1999) 427.
- [52] A. Borodzinski, *Catal. Lett.* 63 (1999) 35.
- [53] P. Albers, K. Seibold, G. Prescher, H. Müller, *Appl. Catal. A* 176 (1999) 135.
- [54] F. Arena, G. Cum, R. Gallo, A. Parmaliana, *J. Mol. Catal. A: Chem.* 110 (1996) 235.
- [55] G. Del Angel, J.L. Benitez, *J. Mol. Catal. A: Chem.* 94 (1994) 409.
- [56] H.R. Adúriz, P. Bodnariuk, M. Dennehy, C.E. Gígola, *Appl. Catal.* 58 (1990) 227.
- [57] S. Asplund, *J. Catal.* 158 (1996) 267.
- [58] M. Larsson, J. Jansson, S. Asplund, *J. Catal.* 178 (1998) 49.
- [59] D. Duca, F. Arena, A. Parmaliana, G. Deganello, *Appl. Catal. A* 172 (1998) 207.
- [60] S. Asplund, C. Fornell, A. Holmgren, S. Irandoust, *Catal. Today* 24 (1995) 181.
- [61] R.K. Edvinsson, A.M. Holmgren, S. Irandoust, *Ind. Eng. Chem. Res.* 34 (1995) 94.
- [62] A.J. den Hartog, M. Deng, F. Jongorius, V. Ponc, *J. Mol. Catal.* 60 (1990) 99.
- [63] J. Houzvicka, R. Pestman, V. Ponc, *Catal. Lett.* 30 (1995) 289.
- [64] D. Lennon, D.R. Kennedy, G. Webb, S.D. Jackson, *Stud. Surf. Sci. Catal.* 126 (1999) 341.
- [65] S.D. Jackson, L.A. Shaw, *Appl. Catal. A* 134 (1996) 91.
- [66] D. Duca, L.F. Liotta, G. Deganello, *Catal. Today* 24 (1995) 15.
- [67] D. Duca, L.F. Liotta, G. Deganello, *J. Catal.* 154 (1995) 69.
- [68] M.A. Aramendia, V. Borau, C. Jimenez, J.M. Marinas, M.E. Sempere, F.J. Urbano, L. Villar, *Stud. Surf. Sci. Catal.* 75 (1993) 2435.
- [69] M.A. Aramendia, V. Borau, C. Jiménez, J.M. Marinas, A. Porras, F.J. Urbano, L. Villar, *J. Mol. Catal.* 94 (1994) 131.
- [70] M.A. Aramendia, V. Borau, C. Jiménez, J.M. Marinas, M.E. Sempere, F.J. Urbano, *Appl. Catal.* 63 (1990) 375.
- [71] A. Bensalem, F. Bozon-Verduraz, *React. Kinet. Catal. Lett.* 60 (1997) 71.
- [72] B.M. Choudary, M.L. Kantam, N.M. Reddy, K.K. Rao, Y. Haritha, V. Bhaskar, F. Figueras, A. Tuel, *Appl. Catal. A* 181 (1999) 139.
- [73] Z.M. Michalska, B. Ostaszewski, J. Zientarska, J.W. Sobczak, *J. Mol. Catal. A: Chem.* 129 (1998) 207.
- [74] C.M. Pradier, M. Mazina, Y. Berthier, J. Oudar, *J. Mol. Catal.* 89 (1994) 211.
- [75] M. Krawczyk, J. Sobczak, W. Palczewska, *Catal. Lett.* 17 (1993) 21.
- [76] A. Borodziński, A. Gołębiowski, *Langmuir* 13 (1997) 883.
- [77] C. Godínez, A.L. Cabanes, G. Villora, *Chem. Eng. Process.* 34 (1995) 459.
- [78] A.N.R. Bos, E.S. Bootsma, F. Foeth, H.W.J. Sleyster, K.R. Westerterp, *Chem. Eng. Process.* 32 (1993) 53.
- [79] A. Borodziński, A. Cybulski, *Appl. Catal. A* 198 (2000) 51.
- [80] C. Godínez, A.L. Cabanes, G. Villora, *Chem. Eng. Commun.* 164 (1998) 225.
- [81] J.C. Fajardo, A.L. Cabanes, C. Godínez, G. Villora, *Chem. Eng. Commun.* 140 (1996) 21.
- [82] J.C. Fajardo, C. Godínez, A.L. Cabanes, G. Villora, *Chem. Eng. Process.* 35 (1996) 203.
- [83] M. Che, C.O. Bennett, *Adv. Catal.* 36 (1989) 55.
- [84] G.C. Bond, *Chem. Soc. Rev.* 20 (1991) 441.
- [85] V. Ponc, *Adv. Catal.* 32 (1983) 149.
- [86] W.M.H. Sachtler, *Catal. Rev.-Sci. Eng.* 14 (1976) 193.
- [87] L. Guzzi, A. Sárkány, in: J.J. Spivey, S.K. Agarwal (Senior Reporters), *Catalysis*, Vol. 11, The Royal Society of Chemistry, Thomas Graham House, Cambridge, 1994, p. 318.
- [88] R. Burch, in: G.C. Bond, G. Webb (Eds.), *Catalysis*, Vol. 7, The Royal Society of Chemistry, Burlington House, London, 1985, p. 149.
- [89] Z. Karpiński, *Adv. Catal.* 37 (1990) 45.
- [90] S. Hub, L. Hilaire, R. Touroude, *Appl. Catal.* 36 (1988) 307.
- [91] J.P. Boitiaux, J. Cosyns, S. Vasudevan, *Appl. Catal.* 6 (1983) 41.
- [92] C.E. Gigola, H.R. Aduriz, P. Bodnariuk, *Appl. Catal.* 27 (1986) 133.

- [93] Yu.A. Ryndin, L.V. Nosova, A.I. Boronin, A.L. Chuvilin, *Appl. Catal.* 42 (1988) 131.
- [94] A. Sárkány, A.H. Weiss, L. Guzzi, *J. Catal.* 98 (1986) 550.
- [95] G. Del Angel, J.L. Benitez, *React. Kinet. Catal. Lett.* 51 (1993) 547.
- [96] F. Ponc, G.C. Bond, *Stud. Surf. Sci. Catal.* 95 (1995) Chap. 11.
- [97] A. Borodziński, R. Dus, R. Frak, A. Janko, W. Palczewska, in: G.C. Bond, P.B. Wells, F. Tomkins (Eds.), *Proceedings of the 6th International Congress on Catalysis*, Chemical Society, London, 1977, p. 150.
- [98] I.T. Caga, E. Shutt, J.M. Winterbottom, *J. Catal.* 44 (1976) 271.
- [99] G. Carturan, G. Facchin, G. Cocco, S. Enzo, G. Navazio, *J. Catal.* 76 (1982) 405.
- [100] W. Palczewska, in: Z. Paál, P.G. Menon (Eds.), *Hydrogen Effects in Catalysis*, Marcel Dekker, New York, 1988, p. 381.
- [101] R.K. Nandi, R. Pitchai, S.S. Wong, J.B. Cohen, R.L. Burwell Jr., J.B. Butt, *J. Catal.* 70 (1981) 298.
- [102] I. Pálínkó, F. Notheisz, M. Bartók, *J. Mol. Catal.* 63 (1990) 43.
- [103] G.C. Bond, *Appl. Catal. A* 149 (1997) 3.
- [104] G. Webb, *Catal. Today* 7 (1990) 139.
- [105] *Catal. Today* 37 (3) (1997) 223–349.
- [106] A.S. Al-Ammar, G. Webb, *J. Chem. Soc., Faraday Trans. 1* 74 (1978) 195, 657.
- [107] S.J. Thomson, G. Webb, *J. Chem. Soc., Chem. Commun.* (1976) 526.
- [108] A. Horváth, A. Beck, L. Guzzi, A. Szűcs, I. Dékány, A. Sárkány, *Catal. Lett.*, submitted for publication.
- [109] S.C. LeViness, Ph.D. Thesis, Rice University, Houston, TX, 1989.
- [110] L. Yayun, Z. Ying, M. Xuern, in: *Proceedings of the Joint Meeting Chem. Eng. Chem. Ind. Eng. Soc. China and Am. Inst. Chem. Eng., Beijing*, 1982.
- [111] Z.E. Gandman, M.E. Aerov, V.A. Men'shchikov, V.S. Getmantsev, *Int. Chem. Eng.* 15 (1975) 183.
- [112] G.C. Battiston, L. Dalloro, G.R. Tauszik, *Appl. Catal.* 2 (1982) 1.
- [113] J. Sheridan, *J. Chem. Soc.* (1945) 133.
- [114] G.C. Bond, J. Sheridan, *Trans. Faraday Soc.* 48 (1952) 651, 658.
- [115] F. King, S.D. Jackson, F.E. Hancock, in: R.E. Malz Jr. (Ed.), *Catalysis of Organic Reactions*, Marcel Dekker, New York, 1996, p. 53.
- [116] S. Bailey, F.E. Hancock, J.S. Booth, Paper, presented at the 8th Ethylene Producers Conference, New Orleans, 1996, Paper 65(e).
- [117] A. Sárkány, A.H. Weiss, T. Szilágyi, P. Sándor, L. Guzzi, *Appl. Catal.* 12 (1984) 373.
- [118] J.P. Boitiaux, J. Cosyns, E. Robert, *Appl. Catal.* 32 (1987) 169.
- [119] P.S. Cremer, G.A. Somorjai, *J. Chem. Soc., Faraday Trans.* 91 (1995) 3671.
- [120] P.S. Cremer, X. Su, Y.R. Shen, G.A. Somorjai, *J. Am. Chem. Soc.* 118 (1996) 2942.
- [121] P.S. Cremer, X. Su, Y.R. Shen, G.A. Somorjai, *J. Phys. Chem.* 100 (1996) 16302.
- [122] A. Sárkány, L. Guzzi, A.H. Weiss, *Appl. Catal.* 10 (1984) 369.
- [123] A.H. Weiss, S. LeViness, V. Nair, L. Guzzi, A. Sárkány, Z. Schay, in: *Proceedings of the 8th International Congress on Catalysis*, Vol. 5, Berlin, 1984, Verlag Chemie, Weinheim, Dechema, Frankfurt am Main, 1984, p. 591.
- [124] P.A. Sermon, M.S.V. Vong, M.A. Martin-Luengo, *Stud. Surf. Sci. Catal.* 88 (1994) 319.
- [125] H.H. Lee, *AIChE J.* 40 (1994) 2022.
- [126] P. Mars, M.J. Goergels, *Chem. Eng. Sci. Suppl., Third European Symposium: Chemical Reaction Engineering*, Pergamon Press, Oxford, 1964, p. 55.
- [127] R. Toei, K. Nakanishi, M. Okazaki, *J. Chem. Eng. Jpn.* 7 (1974) 193.
- [128] T. Haas, C. Otto, J. Gaube, *Dechema Monographie Katalyse*, Frankfurt, 118 (1987) 205–220.
- [129] T. Haas, J. Gaube, *Chem. Eng. Technol.* 12 (1989) 45.
- [130] D. Reinig, D. Honicke, J. Gaube, *Chem. Ing. Technol.* 63 (1991) 839.
- [131] K.M. Deller, in: D.W. Blackburn (Ed.), *Catalysis of Organic Reactions*, Marcel Dekker, New York, 1990, p. 301.
- [132] S. Szabó, *Int. Rev. Phys. Chem.* 10 (1991) 207.
- [133] T. Mallat, A. Baiker, *Catal. Today* 24 (1995) 143.
- [134] T. Mallat, A. Baiker, *Top. Catal.* 8 (1995) 115.
- [135] Z. Bodnar, T. Mallat, I. Bakos, S. Szabo, Z. Zsoldos, Z. Schay, *Appl. Catal. A* 102 (1993) 105.
- [136] H. Lindlar, *Helv. Chim. Acta* 35 (1952) 446.
- [137] A.B. McEwen, M.J. Guttieri, W.F. Maier, R.M. Laine, Y. Shvo, *J. Org. Chem.* 48 (1983) 4436.
- [138] L. Červený, I. Paseka, K. Surma, N.T. Thanh, V. Růžka, *Collect. Czech. Chem. Commun.* 50 (1985) 61.
- [139] W. Palczewska, I. Ratajczykowa, I. Szymerska, M. Krawczyk, in: *Proceedings of the 8th International Congress on Catalysis*, Vol. 4, Berlin, 1984, Verlag Chemie, Weinheim, Dechema, Frankfurt am Main, 1984, p. 173.
- [140] W. Palczewska, A. Jabłoński, Z. Kaszukur, *J. Mol. Catal.* 25 (1984) 307.
- [141] T. Mallat, S. Szabó, J. Petró, *Appl. Catal.* 29 (1987) 117.
- [142] R. Schlögl, K. Noack, H. Zbinden, *Helv. Chim. Acta* 70 (1987) 627.
- [143] J.G. Ulan, E. Kuo, W.F. Maier, R.S. Rai, G. Thomas, *J. Org. Chem.* 52 (1987) 3126.
- [144] J.-P. Boitiaux, J. Cosyns, M. Derrien, G. Léger, *Hydrocarbon Process., Int. Ed.* 64 (3) (1985) 51.
- [145] N.R.M. Sassen, A.J. den Hartog, F. Jongerius, J.F.M. Aarts, V. Ponc, *Faraday Discuss. Chem. Soc.* 87 (1989) 311.
- [146] L. Guzzi, Z. Schay, Gy. Stefler, L.F. Liotta, G. Deganello, A.M. Venezia, *J. Catal.* 182 (1999) 456.
- [147] D.J. Ostgard, K.M. Crucilla, F.P. Daly, in: R.E. Malz Jr. (Ed.), *Catalysis of Organic Reactions*, Marcel Dekker, New York, 1996, p. 199.
- [148] Q. Zhang, J. Li, X. Liu, Q. Zhu, *Appl. Catal. A* 197 (2000) 221.
- [149] M.A. Volpe, P. Rodriguez, C.E. Gigola, *Catal. Lett.* 61 (1999) 27.
- [150] H.R. Aduriz, P. Bodnariuk, B. Coq, F. Figueras, *J. Catal.* 129 (1991) 47.

- [151] H.R. Adúriz, C.E. Gígola, A.M. Sica, M.A. Volpe, R. Touroude, *Catal. Today* 15 (1992) 459.
- [152] Á. Molnár, G.V. Smith, M. Bartók, *J. Catal.* 101 (1986) 67.
- [153] K. Noack, C. Rehren, H. Zbinden, R. Schlögl, *Langmuir* 11 (1995) 2018.
- [154] M. Varga, G. Mulas, G. Cocco, Á. Molnár, *J. Therm. Anal.* 56 (1999) 305.
- [155] K.S. Sim, L. Hilaire, F. Le Normand, R. Touroude, V. Paul-Boncor, A. Percheron-Guegan, *J. Chem. Soc., Faraday Trans.* 87 (1991) 1453.
- [156] Y.H. Park, G.L. Price, *Ind. Eng. Chem. Res.* 31 (1991) 469.
- [157] Y.H. Park, G.L. Price, *J. Chem. Soc., Chem. Commun* (1991) 1188.
- [158] H. Lindlar, R. Dubuis, *Org. Synth. Coll.* 5 (1973) 880.
- [159] J. Barbier, E. Lamy-Pitara, J.P. Boitiaux, P. Marecot, J. Cosyns, F. Verna, *Adv. Catal.* 37 (1990) 299.
- [160] J.P. Boitiaux, J. Cosyns, F. Verna, *Stud. Surf. Sci. Catal.* 34 (1987) 105.
- [161] J.P. Boitiaux, J. Cosyns, G. Martino, *Stud. Surf. Sci. Catal.* 11 (1982) 355.
- [162] J. Yu, J.B. Spencer, *J. Org. Chem.* 62 (1997) 8618.
- [163] J. Yu, J.B. Spencer, *Chem. Commun.* (1998) 1103.
- [164] J.R. Anderson, *Structure of Metal Catalysts*, Academic Press, New York, 1975.
- [165] W.F. Maier, S.J. Chettle, R.S. Rai, G. Thomas, *J. Am. Chem. Soc.* 108 (1986) 2608.
- [166] R.F. Hicks, H. Qi, A.B. Kooh, L.B. Fischel, *J. Catal.* 124 (1990) 488.
- [167] A. Gaussmann, N. Kruse, *Catal. Lett.* 10 (1991) 305.
- [168] A.S. Berenblyum, S.L. Mund, V.V. Karel'skii, *Kinet. Katal.* 26 (1985) 626.
- [169] M.L. Derrien, *Stud. Surf. Sci. Catal.* 27 (1986) 613.
- [170] W. Huang, *Hydrocarbon Process., Int. Ed.* 58 (10) (1979) 131.
- [171] D. Pope, D.S. Walker, R.L. Moss, *J. Catal.* 28 (1973) 46.
- [172] I. Ratajczykowa, I. Szymerska, *Chem. Phys. Lett.* 96 (1983) 243.
- [173] L. Cider, Ph.D. Thesis, Chalmers University of Technology, Goteborg, 1990.
- [174] L. Cider, N.-H. Schöön, *Appl. Catal.* 68 (1991) 207.
- [175] L. Cider, N.-H. Schöön, *Ind. Eng. Chem. Res.* 30 (1991) 1437.
- [176] L. Cider, U. Schröder, N.-H. Schöön, B. Albinsson, *J. Mol. Catal.* 67 (1991) 323.
- [177] Y.H. Park, G.L. Price, *Ind. Eng. Chem. Res.* 30 (1991) 1693.
- [178] J.M. Tour, J.P. Cooper, S.L. Pendalwar, *J. Org. Chem.* 55 (1990) 3452.
- [179] A. Sárkány, *React. Kinet. Catal. Lett.* 68 (1999) 153.
- [180] P. Miegge, J.L. Rousset, B. Tardy, J. Massardier, J.C. Bertolini, *J. Catal.* 149 (1994) 404.
- [181] J.W. Hightower, B. Furlong, A. Sárkány, L. Gucci, *Stud. Surf. Sci. Catal.* 75 (1993) 2305.
- [182] A. Sárkány, *J. Catal.* 180 (1998) 149.
- [183] A. Sárkány, *Appl. Catal. A* 175 (1998) 245.
- [184] J. Goetz, D.Yu. Murzin, R.A. Touroude, *Ind. Eng. Chem. Res.* 35 (1996) 703.
- [185] B. Tardy, C. Noupa, C. Leclercq, J.C. Bertolini, A. Hoareau, M. Treilleux, J.P. Faure, G. Nihoul, *J. Catal.* 129 (1991) 1.
- [186] A. Sárkány, *Appl. Catal. A* 149 (1997) 207.
- [187] A. Sárkány, *Appl. Catal. A* 165 (1997) 87.
- [188] L. Lianos, Y. Debauge, J. Massardier, Y. Jugnet, J.C. Bertolini, *Catal. Lett.* 44 (1997) 211.
- [189] A. Sárkány, Z. Zsoldos, Gy. Stefler, J.W. Hightower, L. Gucci, *J. Catal.* 157 (1995) 179.
- [190] A. Sárkány, Z. Schay, Gy. Stefler, L. Borkó, J.W. Hightower, L. Gucci, *Appl. Catal. A* 124 (1995) L181.
- [191] A. Borgna, B. Moraweck, J. Massardier, A.J. Renouprez, *J. Catal.* 128 (1991) 99.
- [192] J. Phillips, A. Auroux, G. Bergeret, J. Massardier, A. Renouprez, *J. Phys. Chem.* 97 (1993) 3565.
- [193] B.K. Furlong, J.W. Hightower, T.Y.L. Chan, A. Sárkány, L. Gucci, *Appl. Catal. A* 117 (1994) 41.
- [194] J.C. Bertolini, P. Delichere, B.C. Khanra, J. Massardier, C. Noupa, B. Tardy, *Catal. Lett.* 6 (1990) 215.
- [195] A. Sárkány, Z. Zsoldos, B. Furlong, J.W. Hightower, L. Gucci, *J. Catal.* 141 (1993) 566.
- [196] R.S. Monteiro, F.B. Noronha, L.C. Dieguez, M. Schmal, *Appl. Catal. A* 131 (1995) 89.
- [197] A. Sárkány, *Stud. Surf. Sci. Catal.* 111 (1997) 111.
- [198] J. Goetz, R. Touroude, D.Yu. Murzin, *Chem. Eng. Technol.* 20 (1997) 138.
- [199] C. Noupa, J.-L. Rousset, B. Tardy, J.-C. Bertolini, *Catal. Lett.* 22 (1993) 197.
- [200] J. Goetz, M.A. Volpe, R. Touroude, *J. Catal.* 164 (1996) 369.
- [201] T.-B. Lin, T.-C. Chou, *Appl. Catal. A* 108 (1994) 7.
- [202] G.C. Bond, A.F. Rawle, *J. Mol. Catal. A: Chem.* 109 (1996) 261.
- [203] N. Toshima, J. Wang, *Langmuir* 10 (1994) 4574.
- [204] G. Deganello, D. Duca, L.F. Liotta, A. Martorana, A.M. Venezia, A. Benedetti, G. Fagherazzi, *J. Catal.* 151 (1995) 125.
- [205] G. Deganello, D. Duca, A. Martorana, G. Fagherazzi, A. Benedetti, *J. Catal.* 150 (1994) 127.
- [206] A.M. Venezia, A. Rossi, D. Duca, A. Martorana, G. Deganello, *Appl. Catal. A* 125 (1995) 113.
- [207] L.F. Liotta, A.M. Venezia, A. Martorana, G. Deganello, *J. Catal.* 171 (1997) 177.
- [208] M. Varga, G. Mulas, G. Cocco, Á. Molnár, A. Lovas, *Mater. Sci. Eng. A* 304–306 (2001) 462.
- [209] N. Toshima, T. Yonezawa, K. Kushihashi, *J. Chem. Soc., Faraday Trans.* 89 (1993) 2537.
- [210] R. Brayner, G. Viau, G.M. Cruz, F. Fiévet-Vincent, F. Fiévet, F. Bozon-Verduraz, *Catal. Today* 57 (2000) 187.
- [211] E.A. Sales, B. Benhamida, V. Caizergues, J.P. Lagier, F. Fiévet, F. Bozon-Verduraz, *Appl. Catal. A* 172 (1998) 273.
- [212] P. Kukula, L. Červený, *J. Mol. Catal. A: Chem.* 148 (1999) 245.
- [213] H. Miura, M. Terasaka, K. Oki, T. Matsuda, *Stud. Surf. Sci. Catal.* 75 (1993) 2379.
- [214] E.F. Meyer, R.L. Burwell Jr., *J. Am. Chem. Soc.* 85 (1963) 2881.
- [215] B.J. Joice, J.J. Rooney, P.B. Wells, G.R. Wilson, *Discuss. Faraday Soc.* 41 (1966) 223.
- [216] J.J. Phillipson, P.B. Wells, G.R. Wilson, *J. Chem. Soc. A* (1969) 1351.

- [217] G.C. Bond, *J. Mol. Catal. A: Chem.* 118 (1997) 333.
- [218] J.P. Boitiaux, J. Cosyns, E. Robert, *Appl. Catal.* 49 (1989) 235.
- [219] J.P. Boitiaux, J. Cosyns, S. Vasudevan, *Stud. Surf. Sci. Catal.* 16 (1983) 123.
- [220] L.D. Marks, *Surf. Sci.* 150 (1985) 358.
- [221] M. Drechsler, *Surf. Sci.* 162 (1985) 755.
- [222] J. Massardier, J.C. Bertolini, A. Renouprez, in: M.J. Phillips, M. Ternan (Eds.), *Catalysis: Theory to Practice*, Proceedings of the 9th International Congress on Catalysis, Calgary, The Chemical Society of Canada, Ottawa, 1988, p. 1222.
- [223] C.-M. Pradier, Y. Berthier, *J. Catal.* 129 (1991) 356.
- [224] B. Furlong, Ph.D. Thesis, Rice University, Houston, TX, 1996.
- [225] A. Sárkány, *Stud. Surf. Sci. Catal.* 130 (2000) 2081.
- [226] L. Costant, P. Ruiz, M. Abel, Y. Robach, L. Porte, J.C. Bertolini, *Top. Catal.* 14 (2001) 125.
- [227] J.F. Faudon, F. Senocq, G. Bergeret, B. Moraweck, G. Clugnet, C. Nicot, A. Renouprez, *J. Catal.* 144 (1993) 460.
- [228] A. Renouprez, J.F. Faudon, J. Massardier, J.L. Rousset, P. Delichère, G. Bergeret, *J. Catal.* 170 (1997) 181.
- [229] A.C. Mishel, L. Lianos, J.L. Rousset, P. Delichère, N.S. Prakash, J. Massardier, Y. Jugnet, J.C. Bertolini, *Surf. Sci.* 416 (1998) 288.
- [230] J.C. Bertolini, P. Miegge, P. Hermann, J.L. Rousset, B. Tardy, *Surf. Sci.* 331–333 (1995) 651.
- [231] P. Hermann, B. Tardy, D. Simon, J.M. Guigner, B. Bigot, J.C. Bertolini, *Surf. Sci.* 307–309 (1994) 422.
- [232] P. Hermann, J.M. Guigner, B. Tardy, Y. Jugnet, D. Simon, J.-C. Bertolini, *J. Catal.* 163 (1996) 169.
- [233] L. Porte, M. Phaner-Goutorbe, J.M. Guigner, J.C. Bertolini, *Surf. Sci.* 424 (1999) 262.
- [234] J.-C. Bertolini, *Appl. Catal. A* 191 (2000) 15.
- [235] A. Bahia, J.M. Winterbottom, *J. Chem. Technol. Biotechnol.* 60 (1994) 305.
- [236] Y. Furukawa, A. Yokogawa, T. Yokomizo, Y. Komatsu, *Bull. Jpn. Petrol. Inst.* 15 (1973) 56.
- [237] Y. Furukawa, A. Yokogawa, T. Yokomizo, Y. Komatsu, *Bull. Jpn. Petrol. Inst.* 15 (1973) 64, 71.
- [238] J. Oudar, *ACS Symp. Ser.* 31 (1986) 245.
- [239] K.H. Lee, R. Catani, R. Miglio, E.E. Wolf, *Stud. Surf. Sci. Catal.* 111 (1997) 463.
- [240] J.C. Rodríguez, J. Santamaría, A. Monzón, *Appl. Catal. A* 165 (1997) 147.
- [241] K.-H. Stadler, M. Schneider, K. Kochloeff, in: *Proceedings of the 8th International Congress on Catalysis*, Vol. 5, Berlin, Verlag Chemie, Weinheim, Dechema, Frankfurt am Main, 1984, p. 229.
- [242] E.A. Sales, J. Jove, F. Nectoux, F. Bozon-Verduraz, M.J. Mendes, *Hyperfine Interact.* 112 (1998) 13.
- [243] E.A. Sales, M.J. Mendes, F. Bozon-Verduraz, *J. Catal.* 195 (2000) 88.
- [244] J.N. Armor, *Appl. Catal.* 49 (1989) 1.
- [245] V. Gryaznov, *Catal. Today* 51 (1999) 391.
- [246] V.M. Gryaznov, *Platinum Metals Rev.* 30 (1986) 68.
- [247] V. Gryaznov, O.S. Serebryannikova, Yu.M. Serov, M.M. Ermilova, A.N. Karavanov, A.P. Mischenko, N.V. Orekhova, *Appl. Catal. A* 96 (1993) 15.
- [248] A.N. Karavanov, V.M. Gryaznov, N.R. Roshan, I.G. Batyrev, *Kinet. Katal.* 32 (1991) 1045.
- [249] C.K. Lambert, R.D. Gonzalez, *Catal. Lett.* 57 (1999) 1.
- [250] H. Gao, S. Liao, Y. Xu, R. Liu, J. Liu, D. Li, *Catal. Lett.* 27 (1994) 297.
- [251] H. Gao, Y. Xu, S. Liao, R. Liu, J. Liu, D. Li, D. Yu, Y. Zhao, Y. Fan, *J. Membr. Sci.* 106 (1995) 213.
- [252] C. Liu, Y. Xu, S. Liao, D. Yu, *J. Mol. Catal. A: Chem.* 157 (2000) 253.
- [253] C. Liu, Y. Xu, S. Liao, D. Yu, *Appl. Catal. A* 172 (1998) 23.
- [254] C. Liu, Y. Xu, S. Liao, D. Yu, Y. Zhao, Y. Fan, *J. Membr. Sci.* 137 (1997) 139.
- [255] N. Itoh, W.-C. Xu, A.M. Sathe, *Ind. Eng. Chem. Res.* 32 (1993) 2614.
- [256] R.L. Grantom, D.J. Royer, in: W. Gerhartz (Ed.), *Ullman's Encyclopedia of Industrial Chemistry*, 5th Edition, Verlag Chemie, Weinheim, 1987, Vol. 10A, p. 45.
- [257] A. Chauvel, G. Lefebvre, *Petrochemical Processes*, Gulf Publ. Co.-Editions Technip, 1989.
- [258] A.K. Rhodes, D. Knott, *Oil Gas J.* 93 (16) (1995) 33.
- [259] W. Letzsch, *Petroleum Technol. Quart.* (1999) 121.
- [260] H. Singh, S. Pulupala, S.J. Chopra, *Hydrocarbon Technol. Int.* (1998) 21.
- [261] C.L. Hemler, L.L. Upson, *Petroleum Technol. Quart.* (1999) 31.
- [262] J.A. Moulijn, R.A. Sheldon, H. van Bekkum, P.W.N.M. van Leeuwen, *Stud. Surf. Sci. Catal.* 79 (1993) 23.
- [263] R.M. Foley, K.L. Rock, A.S. Bakshi, W. Groten, G. Gildert, D. Weidert, T. McGuirk, *Petroleum Technol. Quart.* (1998) 71.
- [264] F. Trifiro, F. Cavani, *Oxidative Dehydrogenation and Alternative Dehydrogenation Processes*, Catalytica Studies Division, Mountan-View, Study No. 4192OD, 1993.
- [265] D. Sanfilippo, F. Buonomo, G. Fusco, M. Lupieri, I. Miracca, *Chem. Eng. Sci.* 47 (1992) 2313.
- [266] P.R. Pujado, B.V. Vora, *Hydrocarbon Process.* 69 (3) (1990) 65.
- [267] R.O. Dunn, G.F. Schnette, F.M. Brinkmeyer, W. Sund, *Proceedings of DeWitt Petrochem Review*, Houston, TX, 1992, p. 1.
- [268] J.A. Reid, D.R. McPhaul, *Hydrocarbon Process.* 75 (7) (1996) 45.
- [269] B. Didillon, J. Cosyns, C. Cameron, D. Uzio, P. Sarrazin, J.P. Boitiaux, *Stud. Surf. Sci. Catal.* 111 (1997) 447.
- [270] J.P. Boitiaux, C. Cameron, J. Cosyns, F. Eschard, P. Sarrazin, in: M. Baerns, J. Weitkamp (Eds.), *Selective Hydrogenations and Dehydrogenations*, Proceedings of DGMK Conference, Kassel, 1993, p. 49.
- [271] H.M. Allmann, Ch. Herlon, P. Polanek, in: M. Baerns, J. Weitkamp (Eds.), *Selective Hydrogenations and Dehydrogenations*, Proceedings of DGMK Conference, Kassel, 1993, p. 1.
- [272] BASF Catalysts for Ethylene Plants, *Catalyst Brochure*, 1992.
- [273] M.M. Johnson, D.W. Walker, G.P. Nowack, *Europe Patent* 64 301 (1982) to Phillips Petroleum Corp. *Chem. Abstr.* 98 (1983) 160222a.

- [274] K.J. Sasaki, *Petroleum Technol. Quart.* (1997) 113.
- [275] F. Mey, H.-D. Neubauer, R. Schubert, *Petroleum Technol. Quart.* (1997) 119.
- [276] J. Haggin, *Chem. Eng. News* (1993) 21.
- [277] W. König, G. Scharfe, Schmidt, DE-SP Patent 1,062,693 (1957).
- [278] *Petrol. Refiner* 40 (11) (1961) 261.
- [279] W. Krönig, *Hydrocarbon Process.* 49 (3) (1970) 121.
- [280] H. Lauer, *Erdöl Kohle Erdgas Petrochem.* 36 (6) (1983) 249.
- [281] M.L. Derrien, J.W. Andrews, P. Bonnifay, J. Leonard, *Chem. Eng. Progr.* 70 (1) (1974) 74.
- [282] M.C. Convillon, US Patent 4,440,956 (1984) to Dow Chemical Corp. *Chem. Abstr.* 100 (1984) 216459n.
- [283] R.B. Nesbitt, *Feedstock Update*, in: *Proceedings of the 19th Annual Meeting, International Institute of Synthetic Rubber Producers*, 1978.
- [284] J.T. Wehrli, D.L. Thomas, M.S. Wainwright, D.L. Trimms, N.W. Cant, *Stud. Surf. Sci. Catal.* 75 (1993) 2289.
- [285] *Jpn. Patent* 62-23726 (1987), CCN, October 1995.
- [286] S. Chaumette, B. Torck, *Rev. IFP* 49 (6) (1994) 639.
- [287] F. Nierlich, F. Obenaus, *Erdöl Kohle Erdgas Petrochem.* 39 (2) (1986) 73.
- [288] M. Reich, DE-SP Patent 1,184,336 (1963).
- [289] K.H. Walter, W. Droste, F. Nierlich, in: M. Baerns, J. Weitkamp (Eds.), *Selective Hydrogenations and Dehydrogenations, Proceedings of DGMK Conference, Kassel, 1993*, p. 31.
- [290] *Selop Technology, BASF Brochure*, 2000.
- [291] H.G. Müller, Ch. Herlon, G. Meyer, P. Polanek, H. Laib, *Petroleum Coal* 37 (1995) 34.
- [292] M. Derrien, C. Bronner, J. Cosyns, G. Leger, *Hydrocarbon Process.* 58 (5) (1979) 175.
- [293] S. Novolany, R.G. McClung, *Hydrocarbon Process.* 68 (9) (1989) 66.
- [294] A.E. Eleazar, R.M. Heck, M.P. Witt, *Hydrocarbon Process.* 58 (5) (1979) 112.
- [295] R.M. Heck, R.G. Patel, W.S. Breyer, D.D. Merrill, *Oil Gas J.* 81 (3) (1983) 103.
- [296] S. Novalany, R.G. McClung, *Hydrocarbon Process.* 68 (9) (1989) 66.
- [297] C.L. Rogers, *Oil Gas J.* 69 (45) (1961) 60.
- [298] G. Chaput, J. Laurent, J.-P. Boitiaux, J. Cosyns, P. Sarrazin, *Hydrocarbon Process.* 71 (9) (1992) 51.
- [299] *Procatalyse Catalyst Brochure*, 1998.
- [300] G. Gildert, in: M. Baerns, J. Weitkamp (Eds.), *Selective Hydrogenations and Dehydrogenations, Proceedings of DGMK Conference, Kassel, 1993*, p. 59.
- [301] K.L. Rock, R.M. Foley, H.M. Putman, A.S. Bakshi, M. Som, *Petroleum Technol. Quart.* (1998) 51.
- [302] Y.L. Tsai, C. Xu, B.E. Koel, *Surf. Sci.* 385 (1997) 37.
- [303] W.M.H. Sachtler, in: R. Prins, C.G.A. Schuit (Eds.), *The Chemistry and Chemical Engineering of Catalytic Processes*, Elsevier, Amsterdam, 1980, p. 317.
- [304] R.A. van Santen, W.M.H. Sachtler, *J. Catal.* 34 (1974) 202.
- [305] H. Mang, H. Knözinger, B. Breitscheidel, K. Flick, E. Schwab, in: *Proceedings of the 11th International Congress on Catalysis, Baltimore, 1996*, Po-o53.
- [306] S. Arctander, *Perfume and Flavour Chemicals (Aroma Chemicals) II.*, No. 2053, Publ. by the author, Montclair, NY, USA, 1969.
- [307] C.A. Henrick, *Tetrahedron* 33 (1977) 1845.
- [308] E.J. Corey, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 455.
- [309] L.Kh. Freidlin, E.F. Litvin, K.G. Karimov, *Zh. Obshch. Khim.* 44 (1974) 2531.
- [310] P. Kluson, P. Kukula, E. Kyslingerova, L. Červený, *React. Kinet. Catal. Lett.* 59 (1996) 9.
- [311] L. Červený, I. Chloubova, *Seifen, Öle, Fette, Wachse* 116 (1990) 549.
- [312] P. Kukula, L. Červený, *Appl. Catal. A* 177 (1999) 79.
- [313] L.P. Somogyi, *Chem. Ind.* (1996) 170.
- [314] H. Bönnemann, W. Brijoux, A. Schulze Tilling, K. Siepen, *Top. Catal.* 4 (1997) 217.
- [315] BASF A.G. *Eur. Appl.* 412,415A *Platinum Metals Rev.* 35 (1991) 244.
- [316] E.M. Sulman, V.G. Matveeva, L.M. Bronstein, T.V. Ankudinova, E.Sh. Mirzoeva, A.I. Sidorov, P.M. Valetsky, *Russ. Chem. Pharm. J.* 5 (1995) 149.
- [317] E. Sulman, Yu. Bodrova, V. Matveeva, N. Semagina, L. Červený, V. Kurtc, L. Bronstein, O. Platonova, P. Valetsky, *Appl. Catal. A* 176 (1999) 75.
- [318] J. Sobczak, T. Boleslawska, M. Pawlowska, W. Palczewska, *Stud. Surf. Sci. Catal.* 41 (1988) 197.
- [319] P.N. Rylander, in: J.R. Anderson, M. Boudart (Eds.), *Catalysis, Science and Technology, Vol. 4*, 1983, p. 16.
- [320] Linde A.G., *German Appl.* 1/96/25,189; *Platinum Metals Rev.* 42 (1998) 86.
- [321] BASF A.G., *European Appl.* 646,562A, *Platinum Metals Rev.* 39 (1995) 187.
- [322] G.J.K. Acres, A.J. Bird, J.W. Jenkins, F. King, in: J.M. Thomas, R.M. Lambert (Eds.), *Characterization of Catalysts*, Wiley/Interscience, Chichester, 1980, p. 55.
- [323] N. Hsu, L.L. Diosady, L.J. Rubin, *J. Am. Oil Chem. Soc.* 65 (1988) 349.
- [324] E. Santacesaria, P. Parella, M. snm Di Serio, G. Borelli, *Appl. Catal. A* 116 (1994) 269.
- [325] V.I. Savchenko, I.A. Makaryan, *Platinum Metals Rev.* 43 (1999) 74.
- [326] M. Tatsuya, N. Matsuo, *European Pat. Appl.* EP 955,287 to Sumimoto Chem. Comp.; *Chem. Abstr.* 131 (1999) 310403b.