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The Reduction of Alkynes Over Pd-Based Catalyst Materials - A Pathway to Chemical Synthesis

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Abstract

Many reactions, including selective hydrogenation of alkynes, take place on solid surfaces. These reactions are vital in many areas of industry including the manufacture of polymers and fine chemicals such as vitamins, fragrances, and drugs. The choice of a catalyst is a trade-off between activity, selectivity and costs. Palladium-based heterogeneous catalysts are traditionally used for these processes as they provide the activation of hydrogen at room temperatures and offers reasonable selectivity, but these catalysts have a number of practical drawbacks. This review discusses recent research work in the selective hydrogenation of alkynes on palladium-based catalysts, emphasises the mechanism and catalytic materials and important applications including alkyne removal from gas-phase alkene precursors for polymer synthesis and liquid phase selective hydrogenation for the synthesis of fine chemicals. Langmuir-Hinshelwood reaction kinetic models, reaction intermediates, formation of carbonaceous layer, the nature of active sites and the effects of reversible and irreversible adsorbates over Pd surface are discussed as well as the factors affecting catalyst activity and selectivity and how these can be optimised in synthetic protocols for these reactions.

Keywords: Hydrogenation; Selectivity; Alkyne; Alkene; Catalyst; Palladium

Introduction

One of the most important catalytic reactions in organic chemistry is hydrogenation, due to its industrial importance, especially with regards to the synthesis of pharmaceuticals and fine chemicals. In a hydrogenation reaction, a double or triple carbon-carbon bond is saturated with hydrogen giving rise to simple bonds. This reaction is usually performed by molecular hydrogen in the presence of Ni, Pt or Pd catalysts [1,2] either as metallic or bimetallic Pd catalyst unsupported or supported on metal oxides (Figures 1 and 2). The Pd catalysts require the mildest of conditions and therefore are the most widely used. However, if a substrate molecule can withstand high temperatures, Ni may also be used for cost- efficiency [3-6] and it is important to obtain alkene from alkyne (i.e., stop the reaction at the double bond) or hydrogenate a particular double bond or functional group in a diene molecule. This class of reactions is called selective or semi-hydrogenation and may occur in the liquid or gas phase. The last major review of selective hydrogenation was carried out by Molnár et al. [7] and so this review covers more recent studies in the field, including selective hydrogenation in the gas phase (for polymer production) and selective hydrogenation in liquid phase (synthesis of fine chemicals) and concludes by considering future perspectives in this important area of chemistry (Figure 3) and gas-phase selective hydrogenation is important for the polymer industry particularly for polyethylene, polypropylene, styrene and butadiene production. The alkene precursors for these reactions are obtained by catalytic and steam cracking of naphtha or alkylation reactions, which are very unselective reactions producing many side-products, particularly diens and alkynes [7-13]. It is thus important to decrease the amount of side products in the alkene from about 1% to smaller than 5 ppm, because the products poison Ziegler-Natta polymerisation catalysts [7,11]. This can be accomplished by selective hydrogenation of the polymer precursor allowing for the removal of not only alkynes, but also to convert them to valuable alkenes, thus increasing polymer yield [13]. Therefore, the main challenge is to hydrogenate alkynes, but not over- hydrogenate the alkenes. In industry, this reaction is performed over supported catalysts, particularly Pd, Ni or Pd-Ag usually with the addition of carbon monoxide to increase the selectivity to the alkene [7]. Another important application of selective hydrogenation catalysis is the synthesis of fine chemicals such as vitamins, pharmaceuticals, fragrances. For example, semi- hydrogenation is one of the important steps in the synthesis of vitamins A, E, K, the fragrant compound linalool (3,7-dimethylocta-1,6-diene-3-ol) and other products with a worldwide production of more than 1000 tn/yr. [7,14]. An important example is the selective reduction of 2-methyl-3-butyn-2-ol (MBY) to 2-methyl-3-butene-2-ol (MBE) from which vitamins A and E are made.

The main challenge in this industrially important reaction, Figure 4 is to obtain the products in high yield, with high substrate conversion and selectivity, while minimizing reaction duration and the number of reaction and separation steps (such as protection of certain groups, separation of products or catalysts from the product mixture, etc). The catalysts used are based on supported palladium (Pd) nanoparticles and the reaction may be carried out under mild conditions (usually at room temperature), which minimizes adverse reactions of substrates. In order to increase selectivity to the alkene, Lindlar catalyst (Pd poisoned with Pb supported on $CaCO_3$), is widely used although it contains poisonous Pb, which may contaminate the products obtained [15] and extensive research is being undertaken globally to find a suitable replacement for lead in the Lindlar catalyst. In addition, Lindlar catalysts require the optimization of reaction parameters including temperature and pressure even if minor changes are made to substrate structure or if the substrate is changed to another compound [14].

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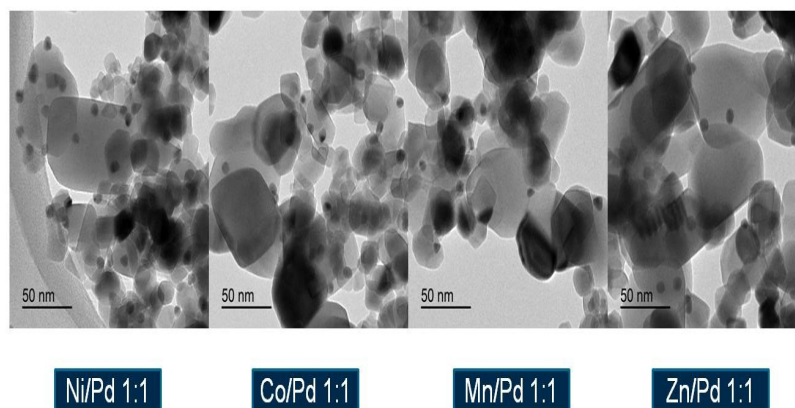
Figure 1: Pd bimetallic particles supported on TiO_2 and obtained by the polyol method with simultaneous application of ultrasound [84].
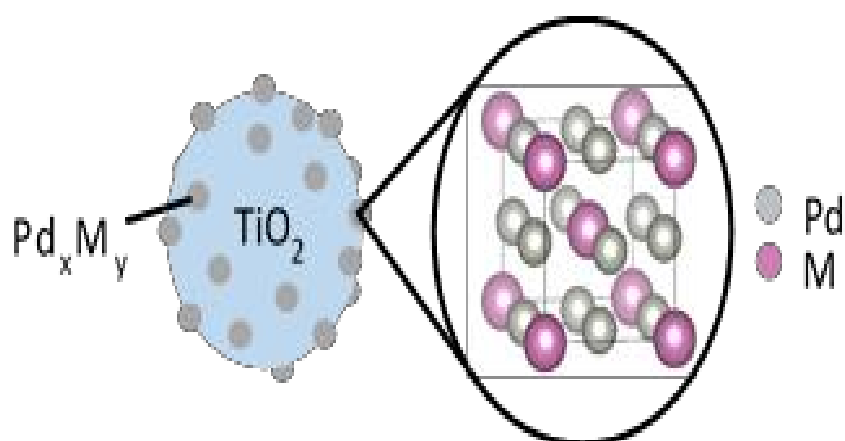

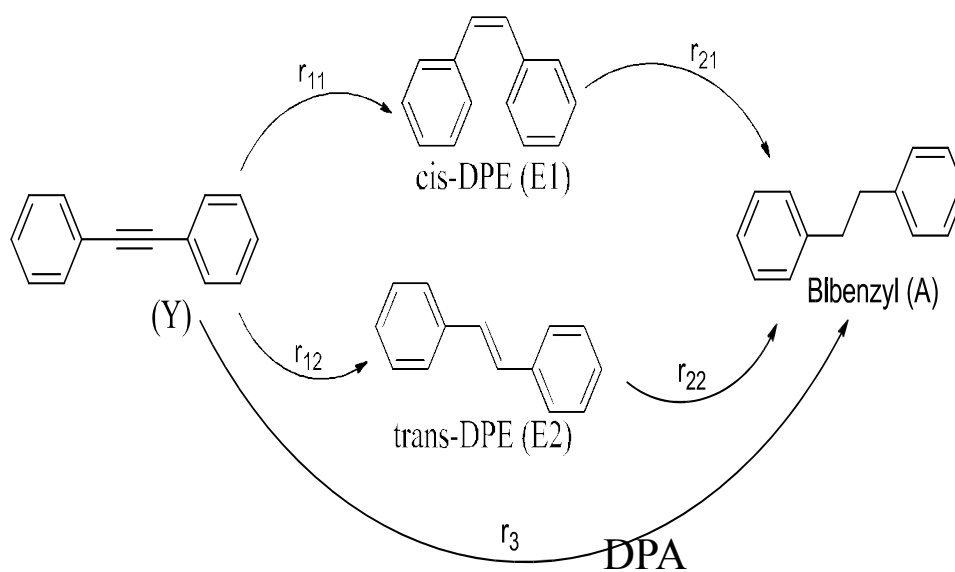**Figure 2:** Structure of intermetallic catalyst system (M=metal) [84].

Figure 3: Diphenylacetylene (DPA) hydrogenation.

As can be seen in Figure 5, Palladium based catalysts have differing levels of performance in terms of selectivity and conversion in MBY hydrogenation, although it is still the predominant catalyst used in selective hydrogenation as is evident from Figure 6 which shows recent research activity using various catalysts including palladium.

The Mechanism of Hydrogenation

Metal catalysts such as Ni, Pt or Pd dissociatively adsorb dihydrogen molecules [1,2] which may further react with substrate molecules forming hydrogenation products. The hydrogenation reaction, as generally accepted, proceeds by Horiuti-Polanyi mechanism: activation of hydrogen and a substrate on the catalyst followed by consecutive addition of hydrogen atoms. This mechanism is confirmed by many experimental works, DFT, and Monte-Carlo simulations [16-18]. The main challenge of selective hydrogenation is to stop the reaction at the alkenes step, i.e., to prevent alkyne over-hydrogenation which is energetically favourable and facilitated by high alkene adsorption energy [19]. In the reaction, palladium hydride is formed in one of two phases - hydrogen poor α-phase and hydrogen rich β-phase. The β-phase is considered to be more active in hydrogenation reactions, but its formation is suppressed by high metal dispersion. It is generally

accepted that the reaction takes place between adsorbed species of a substrate and adsorbed hydrogen. The alkyne adsorbed on the surface of Pd reacts with dissociated hydrogen forming cis-alkene. However, once the alkene is formed, it is easily hydrogenated further to alkane. Therefore, the main challenge for selective hydrogenation is to stop the process at alkene and prevent further hydrogenation to alkanes or other side reactions including oligomerization, as shown in Figure 7.

Selective hydrogenation reactions for the synthesis of fine chemicals is usually performed using Lindlar catalyst, which consists of Pd nanoparticles poisoned with lead on a suitable support such as $CaCO_3$ or activated carbon with typical Pd loading of 5% and 1-2.5% of lead (toxic metal). These catalysts are either used directly or with nitrogen-containing bases, mainly quinoline, which modify their surface properties [17]. Using these catalysts, it is possible to obtain very high conversion and selectivity, of greater than 98% in many cases. However, the catalyst usually deactivates after just one reaction cycle and if water is present in the solvent, the catalyst (and modifying agent) will require separation from the reaction mixture and this entails additional costs [20].

Another approach that is used in the polymer industry to increase
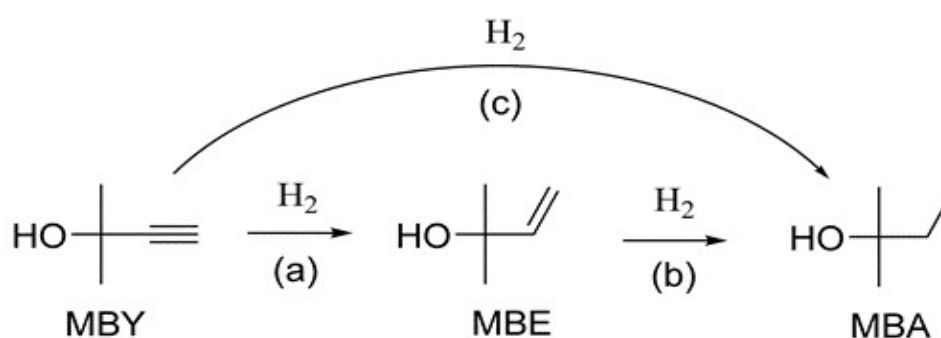

Figure 4: Reaction scheme of the hydrogenation of 2-methyl-3-butyn-2-ol (MBY) to 2-methyl-3- butene-2-ol(MBE) and 2-methylbutan-2-ol (MBA). For selective hydrogenation, step (b) should be avoided and step (c) is not a practical or acceptable option.
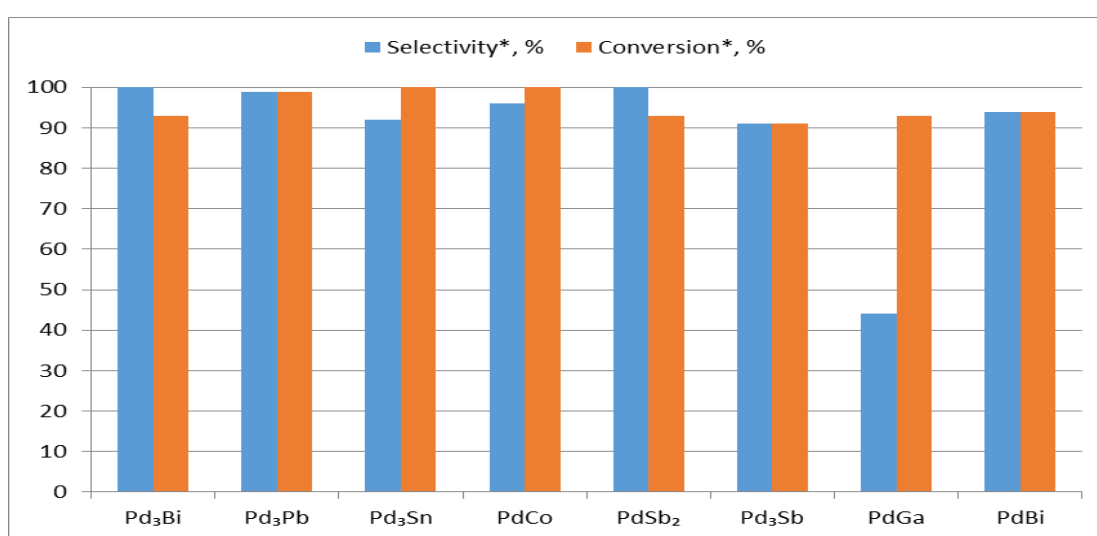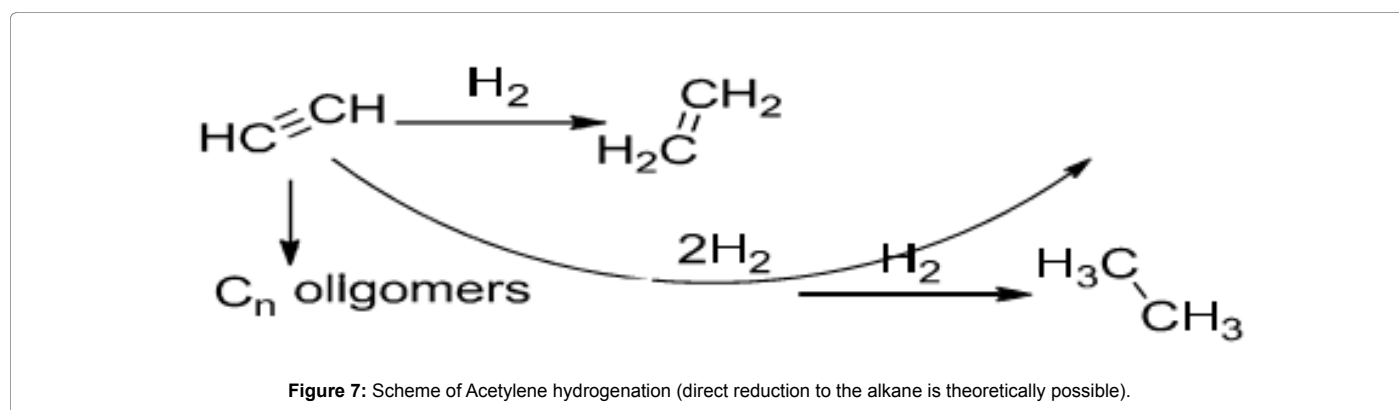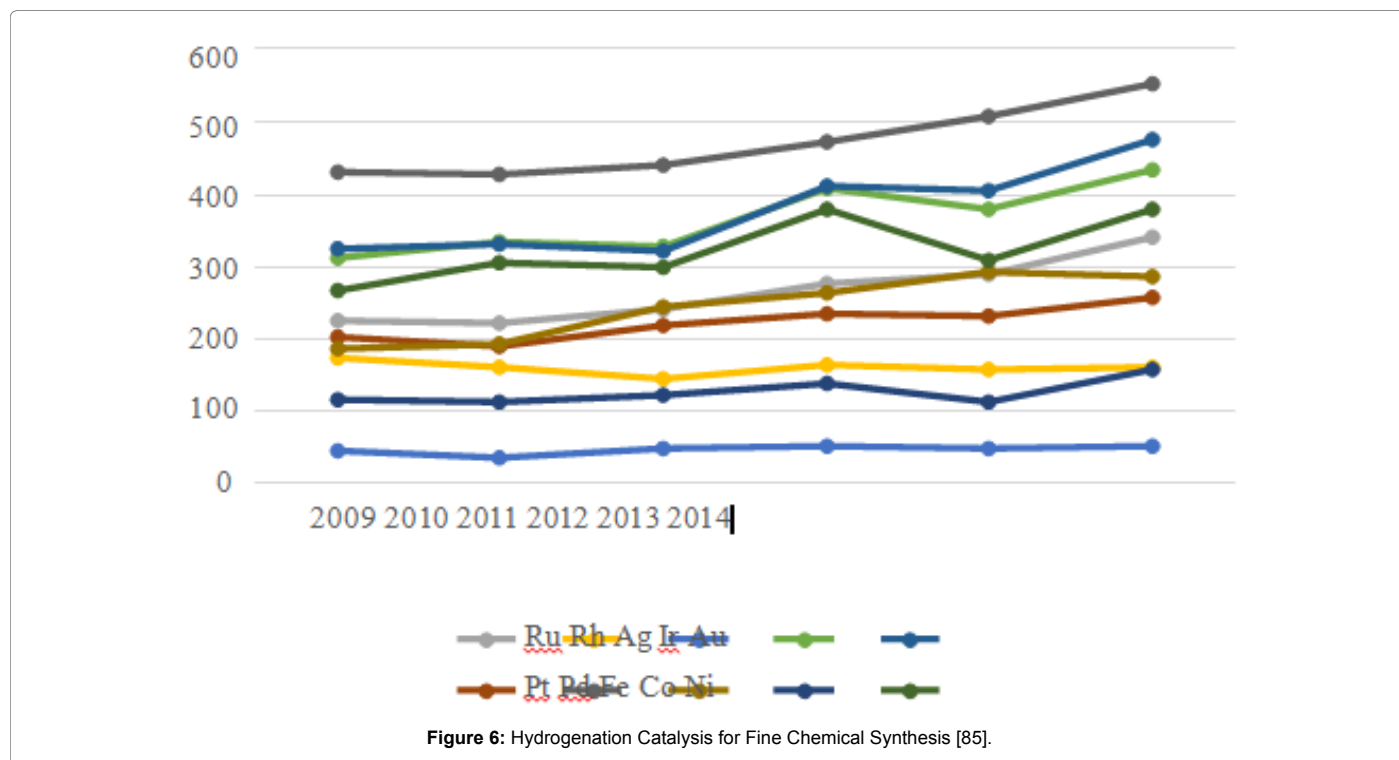

Figure 5: The conversion of 2-methyl-3-butyn-2-ol to 2-methyl-3-butene-2-ol and selectivity of Pd catalysts [84].

Figure 6: Hydrogenation Catalysis for Fine Chemical Synthesis [85].

Figure 7: Scheme of Acetylene hydrogenation (direct reduction to the alkane is theoretically possible).

semi-hydrogenation selectivity is to add CO to the reaction system, which is believed to displace alkene from the adsorption sites of Pd [14,21], although studies have shown that hydrogenation could be reasonably selective (>80%) even on Pd foils without modifications [22,23]. Many authors believe that alkynes adsorb more selectively on a metal surface, retarding alkene adsorption and hindering its hydrogenation to alkane, while alkynes are present in the reaction mixture [17,24]. These explanations imply that the reaction is controlled pure. thermodynamically by adsorption equilibrium. Conversely, there is data contradicting this assumption because ethylene may be hydrogenated even in excess of acetylene [21]. The data demonstrate that there are many types of active sites on the metal surface with different preferred reaction pathways [25-28]. Moreover, both ethylene and acetylene may be adsorbed in various forms on the metal surface and the type of the adsorbed form determines the products - there is a direct path of ethane formation from acetylene through the formation of strongly-bound species such as ethylidyne [14]. This model also explains the effect of CO on the semi-hydrogenation selectivity of alkynes. When CO is introduced to the reaction system, it occupies some adsorption sites on the surface of the metal nanoparticle and decreases the probability of finding free nearby adsorption sites, thus decreasing the number of strongly bound substrate species [14].

There is ample evidence, that at the initial stage of the reaction, dissociative adsorption of substrate molecules takes place forming carbon species. At the second stage, substrate molecules adsorb on this primary layer, i.e., the reaction might not occur on the metal, but on the carbonaceous layer [14].

Jackson and Casey have studied propyne hydrogenation over Pd nanoparticles [29]. At the initial reaction stages, propyne molecules are dissociatively adsorbed and carbonaceous layer is formed on the Pd surface. This layer has a ratio of Pd surface atoms to adsorbed carbon of 1: 3, formed by the adsorbed propyne in di-σ-complex and propilidine forms [29].

In studies by Teschner et al. *in situ* XPS and TEM techniques demonstrated that at the initial reaction stages, carbon species are formed during dissociative adsorption of substrate molecules [30,31]. These species are dissolved in the palladium nanoparticle forming Pd-C surface phase approximately 3 Pd layers thick. The carbide layers play an important role in the hydrogenation, excluding bulk-dissolved hydrogen from the reaction, which otherwise could have over-hydrogenated the substrate molecule. Some Pd facets (e.g., 111) are not prone to carbon dissolution, so hydrogen dissolved in the nanoparticle leads to unselective full hydrogenation. Temperature-programmed desorption (TPD) studies have confirmed that sub-surface hydrogen species lead to non-selective hydrogenation, while surface ones selectively hydrogenate alkynes to alkenes [32]. In addition, according to DFT calculations, the carbide phase affects reaction energetics-only surface hydrogen adsorption is exothermic, but bulk hydrogen dissolution is suppressed in the presence of Pd-C [33]. Sub-surface carbide species, moreover, decrease the adsorption energies of ethylene and acetylene [34] and increase the activation barriers of C-C coupling, hampering oligomerisation and raising alkene selectivity [35]. In order to enhance reaction selectivity towards a particular product (most usually alkene), modifiers are usually added to the reaction system and these may subdivided into two classes: irreversible (metals such as Pb, Cu and Ag) and reversible (quinoline or carbon monoxide) adsorbates. These substances are believed to block some active sites, affect electronic properties, change adsorption energies of the main reactive species and dilute adsorption sites, decreasing the possibility of the formation of strongly bounded species such as ethylidine as in Figure 8 [7,26]. The semi-hydrogenation of MBY to MBE has been used as a test reaction to study the selectivity of novel catalysts as a range of side reactions are possible. One of the important industrial reactions for the multi-tonnage synthesis of polymers, fine chemicals, and vitamins is Pd-catalysed selective hydrogenation. This reaction has been studied for almost a century and its mechanism is widely accepted. At the initial stages of the reaction, substrate molecules and hydrogen are dissociatively adsorbed on the surface of Pd nanoparticle. The surface of Pd is highly dynamic and it is not only surface layers that play an important role in the catalysis, but also its volume. At the initial stages of the reaction, hydrogen forms adsorbed surface layers and dissolves in the Pd, forming hydride phase. Dissociative adsorption of substrate molecules gives rise to the carbonaceous layer over the nanoparticle and Pd-C sub-surface phase with thickness depending on Pd crystallite orientation, hydrogen pressure and other parameters. Hydrogenation occurs not only on Pd surface, but also on the carbonaceous layer. The layer hampers non-selective hydrogenation by the bulk-dissolved hydrogen species. As the formation of the layer takes time, the initial reaction rates do not properly characterise the activity and selectivity of the catalyst. In addition, the surface of Pd, moreover, is very complex because many adsorption forms of substrate molecules are possible on various active sites and the types and number of reactions taking place on these active sites determines the reaction products formed (Figure 9).

In order to maximize selectivity, some active sites on the catalyst surface are poisoned to suppress adverse reactions. In the polymer industry, the poisoning is performed by alloying with Ag and the use of carbon monoxide. In fine chemistry, the poisoning is carried out by the addition of Pb and, sometimes, quinoline. The mechanistic effects of these modifiers are disputed, but it is widely accepted that they perform many functions. Firstly, efficient modifiers enhance thermodynamic selectivity, facilitating preferential adsorption of alkynes and decreasing adsorption of alkenes. Selectivity enhancement is caused by the shift of quasi-equilibrium concentrations of the reactive species on the catalyst
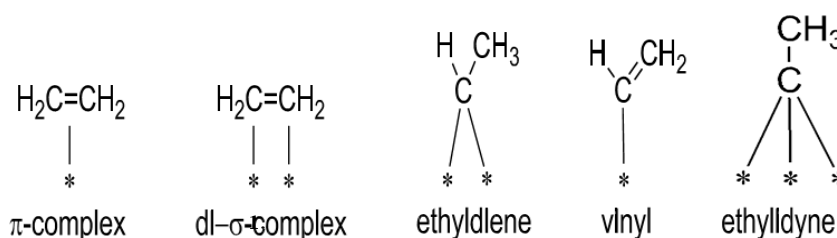

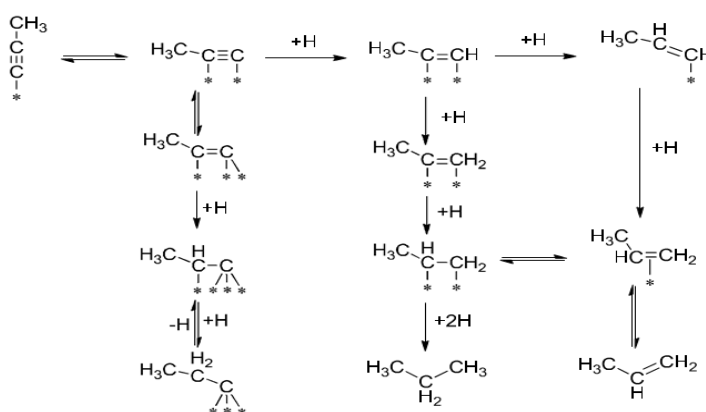**Figure 8:** Adsorption forms of ethylene with an asterisk denoting catalyst adsorption site [14].

Figure 9: Scheme of Propyne hydrogenation, with an asterisk denoting catalyst adsorption site [29].

surface and by the decrease in the rates of side-reactions involving these species rather than by alkene displacement with alkynes. Secondly, adverse active sites are poisoned. The nature and type of these sites depend on the structure and reactivity of a particular substrate molecule -generally, large ensembles of Pd atoms should be avoided, because they facilitate oligomerisation reactions. Along with catalyst poisoning, there are other ways to increase alkene selectivity and this includes the synthesis of the Pd nanoparticles of optimal size, removing mass transfer limitations, decreasing hydrogen pressure and operating at lower alkyne conversion. The optimal diameter of Pd nanoparticles is approximately 5-8 nm; smaller nanoparticles deactivate faster and are prone to passivation by alkynes; while larger particles have smaller fraction of surface atoms. On an industrial scale, hydrogenation for fine chemicals production is performed in batch slurry reactors using Lindlar catalyst. The high toxicity of lead and use of organic solvents are environmentally problems that should be addressed to ensure sustainability.

Gas-phase hydrogenation

In the introductory section of this review, the importance of gas phase hydrogenation was briefly stated. The main challenge of selective hydrogenation of polymer precursors is to decrease alkyne and diene content from ca. 1% to less than 5 ppm and not to hydrogenate valuable alkene to alkane [14-16]. To this end, there are three 3 main directions of the research in this area aimed at increasing selectivity, decreasing catalyst price and enhancing technological convenience. This may be archived by the use of novel catalytic systems and studying the effect of reaction parameters on the yield and selectivity. Even modern computational possibilities require very careful approximations and simplifications in order to estimate the catalytic activity of a given system. Moreover, there are many factors affecting real-life catalytic activity along with the reaction route such as deactivation, sintering, leaching stability and others. Studt et al. have worked on this and proposed NiZn catalyst supported over $MgAl_2O_4$ spinel for the selective hydrogenation of acetylene in a mixture of ethylene [35]. Experimental catalyst testing revealed that NiZn was more selective than industrial catalysts such as Pd and $Pd_{25}Ag_{75}$, producing ca. 10 times less ethane at 99% acetylene conversion. However, the experimental conditions were far from industrial, as very low ethylene content (1.33%) was used instead of an industrial concentration of the order of 20%. Bridier et al. studied multicomponent catalytic systems such as Pd/Al_2O_3, Au/CeO_2, Ni_3Al, Cu_3Al and ternary $Cu_{3-x}Ni_xFe$ in propyne selective hydrogenation [36]. Ternary $Cu_{3-x}Ni_xFe$ showed the highest propene selectivity (93-98%) at 99% propyne conversion when the Ni/(Ni+Cu) ratio was in the range of 8% to 50%. This effect is caused by the reduction of H_2 dissociation barrier over the catalyst, as demonstrated by DFT calculations. However, the experimental conditions adopted in this work were different from industrial conditions as no propene was introduced into the reaction. More often, catalyst systems are tested experimentally to evaluate performance. In this regard, Varga et al. performed the gas-phase hydrogenation of 1-pentyne and 2-pentyne over PdZr and PdCuZr catalysts [37]. PdZr deactivated easily while the PdCuZr showed selectivity of 80-90% to alkene at 100% conversion, with the principal catalyst in these systems being Pd. However, these catalysts required activation with HF to remove surface oxides and must be carefully stored to prevent surface oxidation, which hinders the application of the catalyst. Koeppel et al. used Cu catalysts in the selective hydrogenation of C_4 alkynes and dienes [38]. These catalysts produced no alkanes at all, but, instead, significant amounts (up to 70%) of undesired oligomers were formed. Ota et al. [25] compared Pd_2Ga catalyst with Pd in the selective hydrogenation of acetylene in

excess ethylene (0.5% C_2H_2 and 50% of C_2H_4) [39,40]. The intermetallic catalyst showed a selectivity of 70% as opposed to 20% for Pd catalyst.

Au and Au/Pd nanoparticles were tested in the selective hydrogenation of butadiene in a tenfold excess propene by Hugon et al. [41]. At conversions near 100%, the selectivity to butenes was almost 99%, but all 3 isomers were obtained in comparable quantities due to butane isomerisation. Moreover, Au/Pd nanoparticles were not stable as their surface dramatically changed upon exposure to CO, although under the reaction conditions, hydrogenation activity remained constant for at least 16 h. Nikolaev and Smirnov, studied the selective hydrogenation of acetylene and phenylacetylene in excess of the corresponding alkenes on Au/Ni nanoparticles supported on Al_2O_3 [42]. A strong synergetic effect was observed: the activity of the Au/Ni catalyst was higher than the sum of the activities of the comparable Au and Ni catalysts, which is explained by electron transfer from electron-rich Au to electron-deficient Ni^{2+} moieties.

The effect of reaction parameters and catalyst properties on yield and selectivity is also important in hydrogenation. By 2001, there was ample controversial data on the effect of the size of Pd catalyst nanoparticle on the activity and selectivity. Some authors have claimed that increasing metal dispersion decreases specific activity, while other authors have observed the opposite tendency or that catalyst activity was independent of size [7]. In the recent work by Ruta et al. Pd nanoparticles supported on carbon nanofibers were tested in acetylene hydrogenation [43]. The activity of the 11 nm and 13 nm nanoparticles was 60% higher than the activity of the 8 nm nanoparticles, while the selectivity to ethylene was essentially the same. This effect is ascribed to the faster deactivation rate of smaller particles by carbonaceous species, but not to electronic properties, which is similar to bulk Pd for particles larger than 5 nm [43]. On the other hand, the activity and selectivity of Au/Ni catalyst increased by more than an order of magnitude if nanoparticle diameter decreased from 30 nm to 2.5 nm [42].

Lennon et al. studied the effect of hydrogen concentration on propyne hydrogenation over Pd supported on activated carbon at 298K [44]. Propyne and hydrogen were introduced into the reactor and reaction products were analysed. When hydrogen to propyne ratio increased from 6:1 to 7:1, propyne conversion changed from less than 10% to almost 100%, while propene selectivity sharply decreased. That is, high hydrogen concentration decreases propene selectivity, which is explained by the removal of carbonaceous layer over Pd. Teschner et al. have obtained a similar effect of hydrogen flow rate and studied the Pd/H ratio in the catalyst by gamma activation analysis [39]. This ratio was almost constant in a wide range of hydrogen pressures, but it does not mean that the Pd-H phase is static. On the contrary, this phase is very dynamic as hydrogen substitutes can be replaced by deuterium.

Liquid phase hydrogenation

Hydrogenation in liquid phase differs from gas phase hydrogenation in many respects. Firstly, the supply of the reducing agent to the reaction is usually difficult if the reaction occurs in a multiphase reactor. Secondly, if the reaction is for the synthesis of fine chemicals- the cost of starting materials is considerably higher than that of polymer precursors and the number of possible side reactions is greater due to the complexity of the substrate. Therefore, it is important to obtain high yield, selectivity and to decrease the amount of preparation steps. In this regard, the vast majority of studies are performed using model substrates such as medium-chain alkynes (e.g., hexyne) or multi-functional substrates mimicking industrially important substrates (branched alkyne alcohols such as 2-methyl-3-

butyne-2-ol or 3-methyl- 1-pentyn-3-ol).

Gaseous hydrogen is the cheapest, the most readily available and the most widely used hydrogenating agent. However, its application requires a catalyst and a way for providing efficient hydrogen multiphase transport to the catalyst surface. The latter is done usually by quick stirring in a pressurised batch reactor or a slurry reactor [45]. Another option is to use non catalytic homogenous reduction. Tour and Pendalwar proposed a method of hydrogenation of water-soluble alkynes and alkenes using Pd acetate and $HSi(OC_2H5)_3$ as a hydrogen source, but the yield and selectivity for the hydrogenation of alkynes were quite modest (70-85%) [46]. One important example of liquid phase hydrogenation is the selective reduction of 2-methyl-3-butyne-2-ol (MBY) to 2-methyl-3-butene-2-ol (MBE), an important reaction step in the synthesis of vitamins A and E [17,18].

Along with the hydrogenation to MBE, side reactions are also possible, such as full hydrogenation to MBA, oligomerisation or various isomerisation steps. The main challenge this reaction poses is to perform the hydrogenation of triple bond to double bond, and to prevent further hydrogenation and other side reactions, by using the mildest possible conditions. In this regard, Pd-based catalysts are the most widely used. Protasova et al. [15] reported a method for the selective hydrogenation of MBY using Pd nanoparticles supported over ZnO nanowires without a noble metal [47,48]. The selectivity to MBE was the highest when Pd/ZnO catalyst in methanol was used (selectivity to MBE of 88% at the conversion of 99%). Selectivity to MBE in water decreased to 75% - it is assumed that methanol interacts stronger with alkene molecules hindering their adsorption on metal surface, demonstrating the effect of solvent on selectivity. After the reaction in water or water/methanol mixture, the diameter of ZnO nanowires did not change while the diameter of Pd increased from 2.7 to 3.5 nm. The high selectivity may be explained by the alloying of Pd with Zn. Tew et al. demonstrated that at a temperature as low as 100°C, the formation of Pd/Zn alloy starts and this alloy has a higher selectivity to alkene formation in comparison to un-doped Pd catalyst [49]. But even in the absence of noble metal, ZnO nanowires were catalytically active with selectivity towards MBE as high as 89% in methanol.

Nijhuis et al. studied the catalytic activity of Pd and Pd/Cu -containing catalysts supported on various silica supports (both powdered and monolith) in the reaction of 3-methyl-1-pentyn-3-ol hydrogenation in ethanol solution at 298K and 1100 mbar of H_2 [33]. Using these catalysts, a serial reaction was observed which means that after the formation of alkene, it immediately started to hydrogenate further to alkane, so maximum selectivity was used to compare the catalysts. For Pd catalyst, it was 90.2%, while the use of Pd/Cu catalyst resulted in a 95.3% selectivity and its overall activity decreased from 0.49 to 0.07 mol/gPd min. Cu affects primary adsorption strength of molecules by diluting Pd active sites (ensemble size effect), but the electronic properties are not affected. This dilution decreases the probability of finding many close adsorption sites thus decreasing the amount of strongly adsorbed forms analogous to ethyledine. Lindlar catalyst was also tested in this work and it showed activity similar to that of Cu/Pd catalyst.

The introduction of quinoline is believed to affect the electronic properties of Pd nanoparticles, leading to a decrease adsorption of alkenes. When quinoline is introduced to the reaction system, the kinetics is changed drastically - selective hydrogenation prevails over full hydrogenation to alkane. That is, if quinolone is used, there may be no need to control the reaction mixture to stop it immediately after the formation of an alkene. But this selectivity comes at a price - the reaction rate is decreased 20 times necessitating the removal of quinoline from the reaction product. In this work [33], monolith silica catalyst support was also tried and it was concluded that for the support tested, the activity is most likely to be limited by mass transport which decreased the reaction rates 10 times in comparison to slurry reactors, but the use of monolith catalyst is repaid by easier catalyst separation. Carturan et al. studied the selective hydrogenation of phenylacetylene over alloyed Pd-Pt nanoparticles [50] and a synergetic effect was observed at a Pt content of 20-30%, leading to an increase of the rate constant by a factor of 1.7 and decreased selectivity of alkene formation from 94% for Pd to 91% for $Pt_{18}Pd_{82}$ nanoparticles. Schrock and Osborn applied homogenous Rh-based catalyst for 2-hexyne hydrogenation and provided selectivity of up to 99% of cis-hexene in acetone with reaction rate up to 0.78 mmoles of alkyne reduced per minute [51]. On the other hand, Bianchini et al. used iron-containing homogeneous catalysts for the selective hydrogenation of various acetylene derivatives [52]. The turn over frequency (TOF) was an order of 10 moles of alkyne per mol of catalyst per hour, about 2 orders of magnitude lower than for heterogeneous Pd nanoparticles [33].

Ulan et al. studied the activity of unsupported Pd catalysts in 2-hexyne hydrogenation in hexane under ambient pressure [22]. Pd single crystals and polycrystalline foils were compared and it was shown that terrace Pd surfaces represented the most selective sites for cis-alkene formation. This selectivity appears to originate from a decrease in the rates of side-reactions of cis-alkene (e.g., isomerisation and hydrogenation) with decreasing surface imperfections, although the rate of alkyne hydrogenation was unaffected by different surface orientations.

Mastalir and Kiraly examined the hydrogenation of many alkynes over Pd nanoparticles supported on hydrotalcite anionic clays at 298 K and ambient pressure [53]. Typical parallel reactions were observed as in Figure 10, allowing one to obtain high selectivity of phenylethene of up to 100%, at conversion lower than 87% while selectivity decreased to 85% at higher alkyne conversion. This catalyst demonstrated the highest performance only for 4-octyne, where selectivity was 95% at 99% conversion. Lederhos et al. compared two supports for Pd nanoparticles - pelleted activated carbon and alumina [54]. The nanoparticles had similar dispersions and electronic states on both supports, but the activity of the alumina-supported catalyst was higher, which was proposed to arise from the enhanced shape selectivity in the alumina pores. Papp et al. showed that the structure of MCM-41 degrades on introduction of Pd, but these catalysts were active in various selective hydrogenation reactions giving rise to moderate selectivity and yield [55].

Semagina et al. [56] studied the selective hydrogenation of 2-butyne-1,4-diol over Pd nanoparticles stabilised by poly(ethylene oxide)-block-poly-2-vinylpyridine polymer. This polymer was assumed to combine electron-donating function of pyridine (which decreases ethylene adsorption) with surfactant stabilisation properties of poly (ethylene oxide). Two catalyst materials were studied - unsupported Pd nanoparticles and particles supported on Al_2O_3. Both catalysts were selective to alkene (>99%) up to 94% conversion, but the selectivity decreased to 91% at 99% conversion. Similar catalytic systems were studied in earlier work where more complex alkyne (3,7-dimethyloct-6-ene-1-yne-3-ol) was hydrated by Pd colloid nanoparticles to alkene [57]. Under optimized solution pH and solvent composition, (isopropanol/water mixture), selectivity as high as 99.4% at 100% conversion with TOF=5.7 1/s was achieved. Semagina et al. [58] also deposited monodispersed Pd nanoparticles (ca 8 nm) on a filamentous

support of carbon fibers to make catalyst separation from the reaction mixture easier. The reaction was performed in a batch reactor under H_2 pressure of 1.3 MPa, temperature range of 293-323K using hexane as a solvent and obtained a maximum selectivity of 96% at 90% conversion.

Crespo-Quesada et al. modified Pd nanoparticles with nitrogen-containing bi-pyridinium ligands [59]. These compounds are supposed to act as permanent modifiers, increasing selectivity of 1-hexyne semi-hydrogenation from 88% for non-modified Pd to 98.5% for modified Pd at very low conversion (25%).

Anderson et al. studied the selective hydrogenation of 1- and 2-hexyne over supported Pd/Al_2O_3, $Pd/CaCO_3$, bimetallic $Bi-Pd/Al_2O_3$ and $Pb-Pd/CaCO_3$ catalysts [60]. Along with hydrogenation, complex array of isomerisation reactions of hexene were observed including 'moving' of the double bond and cis-/trans- isomerisation. In the hydrogenation of 1-hexyne, the introduction of Bi to the Pd catalysts does not affect the 1-alkene formation, but further hydrogenation to hexane was more than threefold slower for Bi-doped catalyst. However, traditional Pb-doped Pd catalyst has kinetic characteristics similar to Pb-free Pd catalyst in the reaction of 1-hexyne hydrogenation. On the other hand, for 2-hexyne hydrogenation, the situation is different – the introduction of Pb almost totally blocks non-selective hydrogenation to hexane, but the introduction of Bi barely affects the reaction. Alkynes adsorb and hydrogenate readily both on the flat surfaces and terraces, but alkenes react faster on flat sites due to the steric hindrance of adsorption on terraces. Therefore, Bi preferentially blocks edges and step sites on the Pd nanoparticle, but Pb blocks mostly flat terraces of the Pd nanoparticle.

Along with the composition of a catalyst system, other factors such as nanoparticle size, hydrogen pressure and mass transport limitations play a major role in determining the performance of a catalyst. Although there is contradictory data on the effect of nanoparticle size, Semagina et al. used unsupported Pd particles prepared by reverse microemulsion method and observed that the activity of 1-hexyne selective hydrogenation increased by more than 15 times with a particle size increase from 11 to 14 nm. This effect is ascribed to the necessity of large ensemble of Pd surface atoms to form a hydrogenation active centre, i.e., there are more active centres on the larger nanoparticles [58]. Similar results were reported in other works [61,62]. On the other hand, Anderson et al. demonstrated that nanoparticles of higher dispersion have higher activity [60]. This discrepancy is explained by the adsorption/desorption - limited regime studied in the work by Semagina et al. [56] compared to Anderson et al. who studied the kinetic regimes [60] of the reaction. An increase of hydrogen pressure leads to decrease in alkene selectivity similar to what is observed in gas-phase reactions. At high H_2 pressures, alkyne hydrogenates mainly non-selectively to alkane, while at lower pressure, the rate of hydrogenation is much slower leading to the selective formation of alkenes [23,34,63].

Slow mass transfer may also decrease semi-hydrogenation selectivity. If the reaction is limited by diffusion, over-hydrogenation to alkanes may proceed easier due to slow rate of alkene removal from catalyst pores [33]. High rate of stirring and small catalyst particles are widely used to overcome the diffusion limitations, but there is an elegant and convenient way (Figure 11) to overcome the problem - to use microreactors. Rebrov studied MBY hydrogenation over Pd/TiO_2 and $Pd_{25}Zn_{75}/TiO_2$ catalysts in a microreactor and obtained 90% selectivity to MBE at 99.9% conversion [34]. Moreover, the introduction of quinoline increases selectivity to 97% with no noticeable deactivation during one month time on stream. Natividad et al. obtained selectivity of the semi-hydrogenation of 2-butyne-1,4-diol of up to 99% in the capillary microreactor [63]. Microreactor application not only provided selectivity higher than that which can be obtained in a batch reactor, but it also significantly simplified the process of catalyst separation from the reaction mixture [34], one of the advantages of chemical processing in microreactors.

Langmuir Hinshelwood Kinetics

Metal catalysts such as Ni, Pt or Pd dissociatively adsorb dihydrogen molecules [64] which may further react with substrate molecules forming hydrogenation products. The hydrogenation reaction, as generally accepted, proceeds by Horiuti-Polanyi mechanism: activation of hydrogen and a substrate on the catalyst followed by consecutive addition of hydrogen atoms (Figure 12). This mechanism is confirmed by many experimental works, DFT, and Monte-Carlo simulations [65]. The main challenge of selective hydrogenation is to stop the reaction at the alkenes step, i.e., to prevent alkyne over-hydrogenation which is energetically favourable and facilitated by high alkene adsorption energy [66]. The kinetics of acetylene hydrogenation on Pd catalysts, under ethylene-rich conditions, has been extensively studied and reviewed [67]. Among the models studied, it is difficult to choose one which adequately describes the experimental data. Usually, the kinetics are expressed using exponential expressions – reaction order for hydrogen varies from 0.5 to 1.5 and for acetylene from 0 to -0.5 [68]. More accurate description of the experimental data may be achieved using Langmuir-Hinshelwood-type models with two active sites [69]. For liquid-phase hydrogenation, simpler models are usually used – for example, the mechanism with only one active site consisting of many quasi-equilibrium and rate- determining steps. Many authors assume that the adsorption of hydrogen, substrate and the resulting hydrogenating products are quasi-equilibrium. Moreover, the assumption that these substances compete with each other for active sites of a similar type, describes experimental data much better than the model of independent active sites [70]. There is however no agreement on the particular reaction mechanism used in the modelling. Some authors assume that hydrogen is adsorbed non-dissociatively [71], while other authors assume dissociative adsorption with the second hydrogen atom addition as the limiting step [72] or simultaneous addition of both atoms [72]. DFT calculations suggest that the addition of the second proton to acetylene and ethylene is the slowest step of hydrogenation [65], while Stacchiola et al. assumes that the first protonation is rate-determining [73]. In real systems, depending on the particular substrate and catalyst, a wide pattern of side-reactions is possible, which include oligomerisation of alkyne and alkene, alkene cis-trans isomerisation, double bond shift and other reactions with functional groups (Figure 13).

Effect of Experimental Conditions

Hydrogen concentration significantly affects alkene selectivity and conversion. Lennon et al. demonstrated this non-linear effect in propyne hydrogenation using Pd nanoparticles [44]. When hydrogen to propyne ratio increases from 6:1 to 7:1, the conversion changed from less than 10% to almost 100% and propene selectivity sharply decreased. One of the classical explanations was the formation of hydrogen-rich Pd hydride β-phase, which is much less selective hydrogenation catalyst in comparison to hydrogen-poor α-phase [11]. Conversely, *in situ* prompt gamma activation analysis of this system showed that high selectivity may be achieved even with the β-phase in the presence of carbides because surface, but not bulk; hydrogen species determine selectivity of the reaction [66].

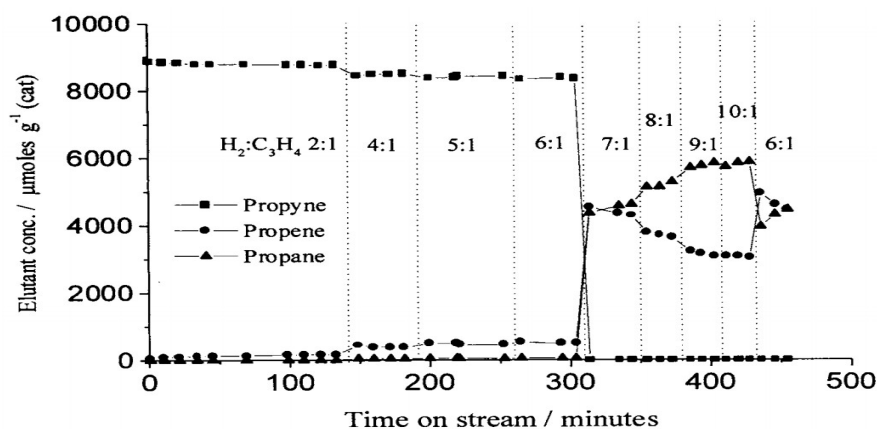Similar tendencies are observed in multiphase hydrogenation

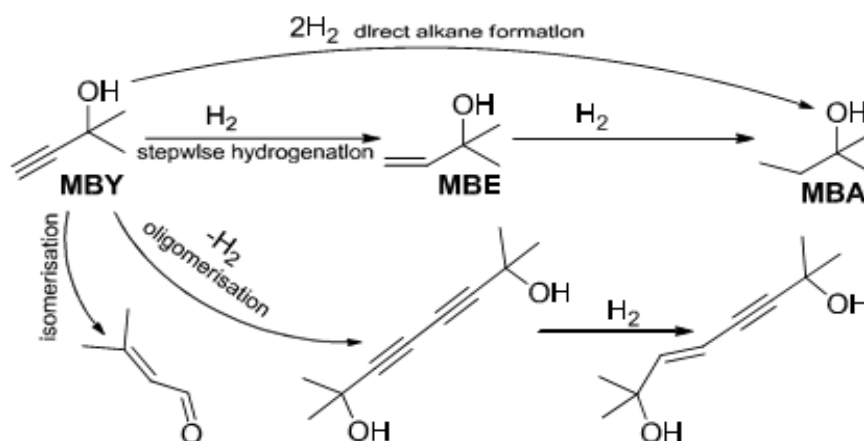**Figure 10:** Product distribution with the increase of hydrogen: propyne ratio from 2:1 to 10:1 [65].

Figure 11: Liquid Phase hydrogenation of hydrogenation of 2-methyl-3-butyne-2-ol (MBY) to 2- methyl-3-butene-2-ol (MBE) and some possible side reactions [18,34]. Direct alkane formation is not a preferred option.
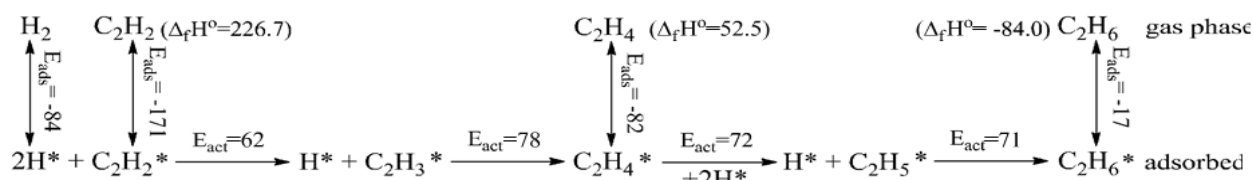

Figure 12: Scheme of the acetylene hydrogenation on Pd catalyst, asterisk denotes adsorbed state. Adsorption and activation energies (in kJ/mol) are taken from DFT calculations [65].

reactions. At high H_2 pressures, alkyne hydrogenates mainly non-selectively to alkane, while at lower pressure, the rate of hydrogenation is much slower leading to the selective formation of alkenes [24,26,37]. Conversely, oligomerisation proceeds faster at low hydrogen to alkyne ratio, so some optimal intermediate substrate to hydrogen ratio is important to achieve high selectivity. The works of Ibhadon et al. on the hydrogenation of MBY using various Pd based catalysts in batch and capillary reactors obtained selectivity and conversions from 95% to 97% depending on the catalyst, catalyst support used and the reactions conditions. The effect of diffusion kinetics on the reaction dynamics was also studied in MBY hydrogenations carried out in tubular reactors with a catalyst coating, enabling the theoretical basis of the flow regimes in the tubular reactor to be validated through experimentation [74].

Effect of particle size

When the size of a nanoparticle decreases, its electronic properties tend to shift to that of a molecule, but these effects are important only for very small particles. For allyl alcohol hydrogenation, electronic effects predominate for nanoparticles 1.3-1.5 nm in diameter, leading to a decrease in the reaction rate [75]. For larger particles, for example, 1.5-1.9 nm, the reaction rate may be described as purely geometric, supposing that it takes place exclusively on the terrace sites of the nanoparticle. Murzin have proposed a model, which describes the geometrical size effects, assuming that the nanoparticle activity is determined by the ratio of step to terrace sites [76]. Recently, Silvestre-Albero et al. carried out a study of model catalysts for the selective hydrogenation of butadiene [77]. The turnover frequency (TOF) of this reaction normalised by the total number of Pd surface atoms is proportional to the particle diameter; but when TOF is normalised by the number of (111) Pd terrace sites, it does not depend on nanoparticle diameter, showing that terrace sites are responsible for semi-hydrogenation for particles larger than 4 nm. For smaller nanoparticles however, the TOF is significantly lower due to surface passivation by strongly adsorbing butadiene molecules, which decrease the amount of available hydrogen atoms. Smaller particles, moreover, deactivate faster [78]. Kiwi-Minsker et al. studied the effects of particle size on alkyne selective hydrogenation. When the diameter of a surfactant-stabilized Pd nanoparticle increased, its activity per surface atom increases [43,86]. Larger nanoparticles (>11 nm) are 3-4 times more active and selective to alkene than smaller particles (6-8 nm). Conversely, Anderson et al. performed the hydrogenation of 1- and 2-hexyne at lower substrate concentrations. Under these conditions, hydrogenation rates are limited by chemical reactions rather than diffusion effects, so at 50% alkyne conversion, when no passivation effects interfere, smaller nanoparticles become more active [52]. Therefore, the picture of irreversible adsorbates and size effects on Pd-catalysed hydrogenation is not yet clear - there is no consensus whether selective hydrogenation prevails over terrace or stepped Pd sites. This disagreement, on the other hand, may suggest that the concept of 'dividing' catalyst surface into only two types of active sites do not provide satisfactory results. This division implies that for any reaction type such as alkyne, alkene hydrogenation and various side-reactions, rates over various terrace sites are similar and rates over defects are very close, although may differ from the rate over terraces. The different behavior of platinum terraces to cis-trans isomerisation reactions indirectly confirms the assumption [60].

Surface modification

There are two main types of modifiers used for Pd surface modification. The first is the introduction of additional metals such as Pb (the most widely used Lindar catalyst), Cu and Ag. Many authors believe that these metals may both affect electronic properties of the Pd and dilute adsorption sites, decreasing the possibility of ethylidine-like species formation as it can lead to non-selective hydrogenation or perform both actions. Second, compounds such as quinoline or pyridine-comprising polymers are used. These substances are believed to block most of the adsorption sites decreasing alkene adsorption due to steric or electron-doping effects of nitrogen [7,22,33,34]. Gislason et al. have performed kinetic simulations of acetylene hydrogenation in ethylene flow under industrial conditions [12]. Although it is wrong to think of reaction kinetics only in terms of activation barriers, the calculations demonstrate that hydrogenation of both acetylene and ethylene proceeds mainly through different mechanistic pathways. The introduction of Ag to the Pd nanoparticles decreases the adsorption barriers of all species thus increasing activation energies. But the largest barrier is further increased in ethylene hydrogenation, thus greatly decreasing the rate of this reaction and increasing the selectivity of acetylene hydrogenation at the cost of decreasing the overall reaction rate (Figure 14). Finally, the two main conclusions important for the development of selective hydrogenation catalysts can be summarised as follows:

(1) The surface of Pd is very complex and contains many types of active sites on which different reactions occur and these may decrease reaction selectivity. Therefore, it is essential to modify the Pd surface to block these 'adverse' sites.

(2) The Pd catalyst is highly dynamic and it is not only surface layers that play important role, but also the volume. At the initial stages of reaction, the catalyst adjusts to the substrate by forming carbonaceous layer over its surface and the activity and selectivity might be low at this point.
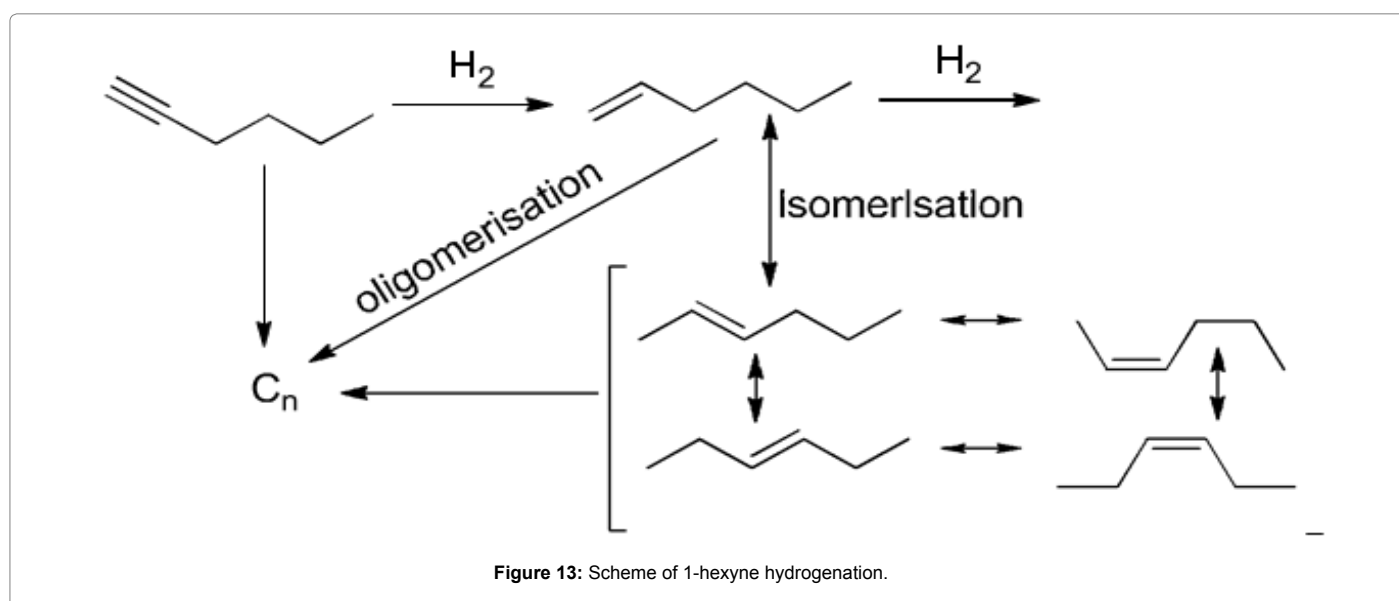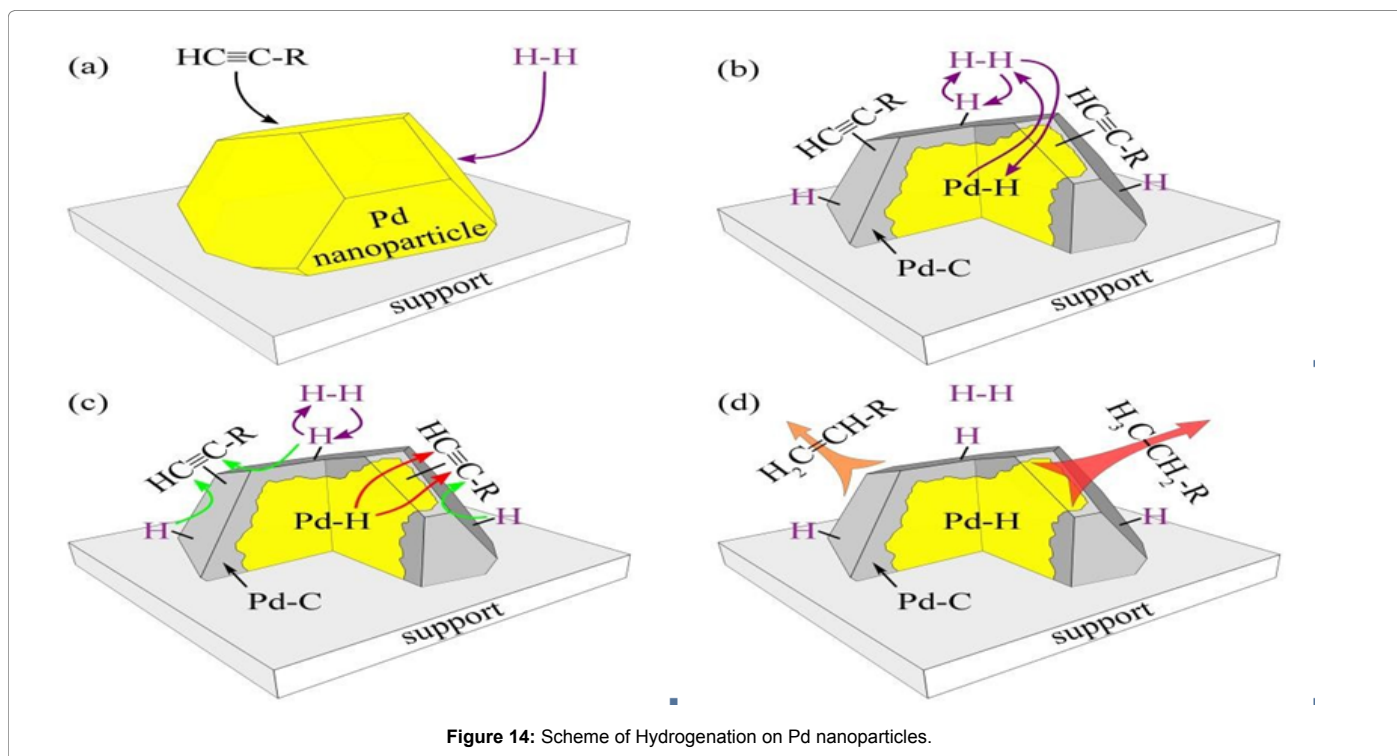

Figure 13: Scheme of 1-hexyne hydrogenation.

Figure 14: Scheme of Hydrogenation on Pd nanoparticles.

Reversible adsorbates

Selective hydrogenation for fine chemicals synthesis is usually performed with Lindlar catalyst - Pd nanoparticles poisoned with lead on a suitable support such as $CaCO_3$ or activated carbon. This catalyst is either used directly or with the addition of nitrogen-containing bases (mainly quinoline), which modify the surface properties to achieve selectivity up to 98% at high conversion [74]. The reasons for these effects are many and usually cannot be described only by thermodynamic equilibrium factors, electronic effects or active site poisoning [75]. García-Mota et al. performed DFT study of the Lindlar catalysts and showed that modifiers, lead and quinoline, cause twofold effects [77]. First, both modifiers reduce alkene adsorption energy which decreases the possibility of side-reactions and second, larger quinoline molecules and smaller Pb atoms tile Pd surface leaving only few isolated active sites available. Spatial separation of the sites suppresses C-C bond formation or oligomerization reactions, enhancing semi-hydrogenation selectivity. On the other hand, the strong adsorption of quinoline on the Pd surface is likely to be caused by its large delocalised π-electron areas rather than its basic properties, because adsorption energy of naphthalene is comparable to that of quinoline, but is much higher than that of pyridine [76]. Alkylamine modifiers, similarly, enhance thermodynamic factors for Pt and $CoPt_3$ nanoparticles – amines with carefully chosen alkyl chain length suppress alkene adsorption and thereby increase selectivity.

After the reaction, the products must be separated from the catalyst, with quinoline requiring an additional step of distillation or recrystallization and pushing up the production costs and, for some substrates, depending on their properties, the separation is almost impossible. Therefore novel modifications are needed, which not only increase reaction selectivity, but provide for easier separation from the products. Many nitrogen and sulphur-containing polymers show exceptional selectivity at high activity [27,62,63]. It is likely that these modifiers combine active site poisoning, electronic and thermodynamic effects, although the mechanistic details are not clear.

Another approach used in the polymer industry to increase alkyne and diene semi-hydrogenation selectivity, is to add CO to the reaction system. Its effect is usually ascribed to the displacement of alkenes from the Pd adsorption sites, i.e., the effect is purely thermodynamic [78]. Recent experimental and theoretical studies show that CO has a twofold effect [79]. First, even small concentrations of CO enhance thermodynamic effects and decrease alkene adsorption. Second, the formation of a CO adsorption layer decreases hydrogen surface concentration to a level, which is sufficient for diene and alkyne hydrogenation, but not enough for subsequent alkene hydrogenation to alkanes [80].

Irreversible adsorbates

It is widely accepted that irreversible adsorbates, such as lead in a Lindlar catalyst, preferentially block some active sites on Pd nanoparticles, therefore studies of active sites are inevitably connected to the effects of irreversible adsorbates. Ulan et al. compared the semi-hydrogenation activity of (111), (100) and (100) Pd crystalline facets which have various proportions of kink and step sites (Pd atoms with coordination numbers 6 and 7, respectively) to terrace sites (coordination numbers are 8 or 9) [22]. Terrace atoms were reported to be the most selective in 2-hexyne semi-hydrogenation, with selectivity originating from suppressing other side-reactions rather than accelerating the reaction rate [81]. Now, it is widely accepted that Pd terrace atoms provide more selective semi-hydrogenation and these results have been indirectly confirmed by other experimental studies, where selectivity was compared for nanoparticles of various sizes (larger nanoparticles naturally contain a lower fraction of terrace sites than smaller particles [7,46,47]. Based on these data, many authors explain the enhanced selectivity of lead- doped Pd nanoparticles as due to the preferential adsorption of lead on the step and kink sites [82]. Recent

DFT calculations further confirm the conclusions that lead atoms are adsorbed stronger on the step sites than on terrace sites [48,49].

Recently, Crespo-Quesada et al. obtained Pd nanoparticles of various sizes and shapes (cubes, octahedra and cubooctahedra) and showed that over-hydrogenation prevails on step and kink sites, but semi- hydrogenation preferentially occurs on the terrace Pd atoms [59]. The authors, however, admit that the stabilizing agent, poly (vinyl pyrrolidone), may be found on the catalyst nanoparticles and can modify the properties of the catalyst surface. Step atoms were reported to be four times less active compared to terrace ones; but it is interesting to note that a previous study showed that the full removal of the stabilizing agent by means of ultraviolet-ozone treatment increases activity four times [50]. This coincidence in numbers may indicate that the reported preference of terrace sites characterises not the Pd nanoparticle itself, but a complex of the Pd nanoparticle and an adsorbed stabilizing agent. That the polymer preferentially adsorbs on the step sites and decreases the hydrogenation rates on these sites. Preferential adsorption of the polymer on the defect sites of platinum supports indirectly this assumption [51].

Conversely, Anderson et al. performed a study of 1- and 2-hexyne hydrogenation and showed that the products for Bi- and Pb-doped Pd catalysts differ. These modifiers do not affect the rate of hexyne semi-hydrogenation, but significantly affect the rates of side reactions: Pb suppresses cis-trans isomerisation of 2-hexyne, while Bi suppresses the double bond shift reactions in hexene. Comparisons of the IR spectra of CO-adsorbed catalysts demonstrate that Bi preferentially adsorbs on the step and kink sites, while Pb blocks terrace sites [60]. These data cast doubt on the established concepts of higher selectivity of terrace Pd atoms. Moreover, preferential adsorption of Bi on step sites of Pt (775) facets [53] indirectly confirms the findings.

López and Vargas-Fuentes have recently reviewed the properties of various metal adsorbates for Pd catalysts from the point of view of energetics using DFT and considering the stability of the alloyed materials and the preference of adsorbates for step sites [49]. The properties of Pb and Bi are surprisingly similar - they tend to disperse on the surface due to repulsion and preferentially adsorb over step sites rather than terraces. These results contradict our experimental data – either due to the formation of meta-stable structure during the synthesis of Bi-doped catalysts or factors such as the presence of oxygen was not taken account of in DFT calculations.

From another perspective, Gislason et al. [12], performed kinetic simulations of acetylene hydrogenation in ethylene flow under industrial conditions and showed that the introduction of Ag to the Pd has twofold effect. It (a) decreases the desorption energy of acetylene and ethylene and (b) increases the activation energies of all hydrogenation reactions - both these effects enhance alkene selectivity. Kinetic simulations also show that the classical explanation of selectivity as originating from the displacement of ethylene by acetylene in acetylene hydrogenation does not fully describe the system because acetylene surface coverage is always low. Similar conclusions were derived from DFT calculations – the presence of Pb in reactions catalysed by Pd decreases the adsorption energies of ethyne and ethene, rendering Pd atoms situated close to the Pb almost inactive in full hydrogenation [83,84].

Conclusions

The addition of hydrogenation to carbon-carbon double or triple bonds is an important reaction for industry as it forms the bedrock for the synthesis of a vast array of chemicals and pharmaceutical ingredients. The growing need to manufacture chemicals at reduced cost, develop green processes and ensure environmental safety calls for continued innovative, competitive and versatile techniques to reduce energy use, increase yield and selectivity in the synthesis of chemicals via selective reduction reactions. The development and use of novel catalysts, reactors and flow methodologies are important in achieving these objectives. In this regard, continuous flow hydrogenation technology has attracted the attention of the research community both as an enabling tool to enhance organic synthesis and as a manufacturing method that could potentially reduce processing costs, add to environmental safety and reduce energy use [85-88]. Consequently, it has been ranked as a high priority research area for pharmaceutical and fine chemicals manufacturing and significant progress has been made in establishing these methods for the production of important target compounds and valuable synthetic building blocks. In addition, the miniaturisation of chemical reactors should offer many fundamental and practical advantages to the pharmaceutical industry that are constantly searching for controllable, information-rich, high-throughput and environmentally friendly methods of producing products with a high degree of chemical selectivity. To develop a new generation of drugs, industries need to be able to synthesise and screen chemicals with enhanced speed, and a new technology that enables a cost-neutral step change in the number of potential drug candidates would provide a distinct competitive advantage. In this regard, catalyst selectivity and activity are critical requirements and it is desirable for reactions to provide semi hydrogenated product with minimal over hydrogenation, reduced content of toxic metals, such as lead as well as the content of scarce metals including palladium.

One of important steps in the industrial multi-tonnage synthesis of polymers, fine chemicals, and vitamins is the reaction of Pd-catalysed selective hydrogenation. The reaction is studied for almost a century; its principal mechanism is widely accepted. Schematically, at the initial stages of the reaction, substrate molecules and hydrogen are dissociatively adsorbed on the surface of Pd nanoparticle, Surface of Pd is highly dynamic and not only surface layers play essential role in the catalysis, but also its volume. At the initial reaction stages, hydrogen forms adsorbed surface layers and dissolves in the Pd, forming hydride phase. Dissociative adsorption of substrate molecules gives rise to the carbonaceous layer over the nanoparticle and Pd-C sub-surface phase with the thickness depending on the Pd crystallite orientation, hydrogen pressure and other parameters. Hydrogenation occurs not only on Pd surface, but on the carbonaceous layer; the layer hampers non-selective hydrogenation by the bulk-dissolved hydrogen species. Formation of the layer takes some time, so initial reaction rates do not properly characterise activity and selectivity of the catalyst. Surface of Pd, moreover, is very complex because many adsorption forms of the substrate molecules are possible on various active sites; combination of reactions taking place on these active sites determines the reaction products.

In order to maximize selectivity, some active sites on the catalyst surface should be poisoned to suppress adverse reactions. In polymer industry the poisoning is performed by alloying with Ag and introduction of carbon monoxide; for fine chemistry – addition of Pb and, sometimes, quinoline. Mechanistic effects of these modifiers are disputed, but it is widely accepted that they perform several essential actions. Firstly, efficient modifiers enhance thermodynamic selectivity, facilitating preferential adsorption of alkynes and decreasing adsorption of alkenes. Selectivity enhancement is caused by the shift of quasi- equilibrium concentrations of the reactive species on the catalyst surface and by decrease of the rates of side-reactions involving

these species rather than by alkene displacement with alkynes; thermodynamic factors cannot be considered as the only reason of selectivity. Secondly, adverse active sites should be poisoned. Type of these sites depends on the structure and reactivity of a particular substrate molecule; generally, large ensembles of Pd atoms should be avoided, because they facilitate oligomerisation reactions. Along with catalyst poisoning, there are some other ways to increase alkene selectivity such as the synthesis of the Pd nanoparticles of optimal size, removing mass transfer limitations, decreasing hydrogen pressure and operating at lower alkyne conversion levels. The optimal diameter of Pd nanoparticles is approximately 5-8 nm, smaller nanoparticles deactivate faster and are prone to passivation by alkynes whereas larger particles have a smaller fraction of surface atoms. While technological optimisation is far from being exhausted, environmental concerns still persist with respect to the use of lead doped $Pd/CaCO_3$ catalyst [89-92].

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