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Catalytic hydrogenation of alkyne and alkadiene impurities in alkenes. Practical and theoretical aspects

S A Nikolaev, L N Zanaveskin, V V Smirnov, V A Averyanov, K L Zanaveskin

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Abstract. Catalytic systems for selective hydrogenation of highly unsaturated impurities (dienes and alkynes) in hydrocarbon streams are considered. Nano-sized bimetallic catalysts based on palladium or gold are shown to be the most promising catalytic systems. The bibliography includes 162 references.

I. Introduction

Alkenes (first of all, ethylene, propylene, but-1- and -2-enes, isobutene, isopentene, styrene and α-methylstyrene) are important raw materials for the industrial organic synthesis. The main application fields of ethylene include large-scale production of polyethylene, poly(vinyl chloride), ethylene oxide, ethanol, acetaldehyde, vinyl acetate and polymers based on it, ethylbenzene, and so on.[1–4] Propylene is used to produce polypropylene and new polypropylene-based materials, to synthesize propylene oxide, acrylonitrile, isopropyl alcohol and other products.[1–4]

S A Nikolaev, V V Smirnov Department of Chemistry, M V Lomonosov Moscow State University, Leninskie Gory, 119991 Moscow, Russian Federation. Fax (7-495) 939 88 46, tel. (7-495) 939 34 98, e-mail: serge2000@rambler.ru (S A Nikolaev), akagi@hotbox.ru (V V Smirnov)
L N Zanaveskin, K L Zanaveskin State Centre of Science of the Russian Federation L Ya Karpov 'Research Physical and Chemical Institute', ul. Vorontsovo pole 10, 105064 Moscow, Russian Federation. Fax/tel. (7-495) 735 65 39, e-mail: zanaveskin@list.ru (L N Zanaveskin), zakon82@mail.ru (K L Zanaveskin)
V A Averyanov L N Tolstoy Tula State Pedagogical University, prosp. Lenina 125, 300600 Tula, Russian Federation. Fax (7-4872) 24 73 64, tel. (7-4872) 35 78 08, e-mail: piligrim.tula.ru@gmail.com

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An increasing demand of industry for ethylene and propylene is demonstrated by the dynamics of growth of their world output. Indeed, about 1 mln tonnes of ethylene was produced in 1950,[5] 80.5 mln tonnes, in 1998,[6,7] and the output predicted for 2010 is 120 mln tonnes.[8] The increase in the world output of propylene is even more rapid, namely 5% per year against 3.5% for ethylene. In 1998 its output was 47 mln tonnes and the value predicted for 2010 is 82 mln tonnes.[8]

But-1- and -2-enes, isobutene and isopentene are also important hydrocarbon raw materials used in various fields of industrial organic synthesis. In particular, but-1-ene is used as a comonomer in the manufacture of linear low-density polyethylene and is a reagent in the synthesis of *sec*-butyl alcohol, maleic anhydride, polybutylene; but-2-ene is an excellent alkylating agent for the production of high-octane petrols, ethyl methyl ketone and maleic anhydride.[3,9] The main application field of isobutene and isopentene is the synthesis of *tert*-butyl methyl and *tert*-pentyl methyl ethers, respectively, which are added to petrol to increase the octane number and exclude formation of highly toxic products upon combustion.[3,9] Isobutene is widely used to produce various brands of polyisobutylene and butyl rubber; it is the starting compound in the synthesis of isoprene, *tert*-butyl alcohol, *tert*-butylamine and other valuable products.[1,9,10] Styrene is used in the production of polystyrene, its copolymers and synthetic rubbers.[1,5]

The industrial synthesis of unsaturated hydrocarbons usually includes cracking of petroleum alkanes starting with light gas fractions C_2-C_3 and ending with heavy liquid fractions such as naphtha and gas oil.[3,4] Depending on the type of feed, the availability of power resources and technological traditions, thermal, steam or catalytic cracking and dehydrogenation are employed. Thus, styrene production process is based on dehydrogenation of pure ethylbenzene. Due to the need to suppress the undesirable

destruction of carbon–carbon bonds, catalytic cracking is the process of choice. However, heavy hydrocarbon fractions are cracked at high temperatures without a catalyst, which favours destruction of heavy hydrocarbon molecules, resulting ultimately in valuable light alkenes such as ethylene and propylene. The impurities of alkynes and dienes inevitably formed in these processes are highly undesirable, as they irreversibly deactivate the catalysts used in subsequent processing of the alkenes formed. For example, during stereoregular polymerization of ethylene and styrene, these impurities rapidly poison the Ziegler–Natta catalysts and sharply decrease the quality of the resulting polymers. They affect similarly the catalytic systems used in other processes.[9] Therefore, the contents of alkyne and diene impurities in the starting alkene should be reduced down to the minimum admissible value, which is 10, 5, 2 or even 1 ppm depending on the final processing product.[11–20] This problem arises in the synthesis of buta-1,3-diene where the dehydrogenation products of the butane–butene fraction contain, apart from the target diene, the undesirable impurities of highly unsaturated compounds, but-1- and -2-yne, vinylacetylene and other.[21,22]

The removal of such impurities by fractional distillation is uneconomic, as it requires high energy and capital expenditures.[21–25] Selective adsorption of acetylene on zeolites has been suggested for isolation of acetylene from an ethylene stream;[19] however, this suggestion was not supported by testing results. The selective catalytic hydrogenation of alkynes and dienes without involvement of alkenes is the most promising and, to an extent, approved method for purification of alkene-containing hydrocarbon streams from these impurities.[11–19,26] The advantage of this process is that the impurity alkynes and dienes are converted into the target alkenes; therefore, no additional processing is required after the hydrogenation stage.

Increasing the efficiency and the selectivity of hydrogenation of highly unsaturated impurities in the hydrocarbon streams implies task-specific approach to the selection of the catalytic system, which should satisfy a particular set of requirements. These include

(1) high catalyst activity in the hydrogenation, which allows bringing the impurity conversion to almost 100%;

(2) high catalyst selectivity with respect to alkene (not lower than 80%, desirably 95%–99%);

(3) stability of catalyst operation;

(4) insensitivity of the catalyst to poisoning by reaction products;

(5) easy preparation and regeneration and low cost of the catalyst.

II. Catalysts for selective hydrogenation

The studies carried out in the last decades have shown that hydrogenation processes of highly unsaturated compounds in hydrocarbon streams can be implemented more or less successfully on supported metal catalysts in which d metals serve as active components. Metals active in the selective hydrogenation include palladium,[14,15,17,20,25–42] nickel,[13,21,27,28,43] platinum,[13,27,28,44] copper,[13,21,23,28,45] silver,[13,21,28,46] gold,[13,47,48] rhodium,[13,28,49] iridium,[28] tin,[28] cobalt,[13,21,45] chromium,[13,21] manganese,[21] iron [13] and ruthenium.[13]

In recent years, increasing attention has been paid to catalytic systems based on bimetallic compositions, since they are more active, selective and stable against various types of deactivation. The tested bimetallic compositions include Pd–Ag,[11,12,17,27,28,38–40,46–60] Pd–Au,[20,27,28,39,46,55,60,61] Pd–Co,[28,39,55] Pd–Ni,[28,40,45,55] Pd–Cr,[40,62,63] Pd–Cu,[22,27,28,39,40,46,55] Pd–Sn,[28,53,55] Pd–Zn,[13,20,27,28,53] Pd–Pb,[40,53,64] Pd–Fe,[28] Pd–Si,[39,40,65] Pd–Cd,[53] Pd–Hg,[53] Pd–Te [40] and Pd–Ga systems;† nickel alloys with chromium, gold, rhodium, ruthenium, copper, palladium and cobalt,[13,21,66–68] and platinum alloys with silver, cobalt, nickel, copper, tin and gold.[21,22,27,55] The supports used for the metal and bimetallic catalysts comprised various modifications of alumina (γ, β, η, δ, θ, α) and their mixtures;[11,18,21–36,44,45,50,51,66–70] silica;[19,21,26,32,38,45–47,61] aluminosilicates;[22,33,52] titania;[21,26,38–40,46–48,66,71,72] zirconia;[22,27,32,51,70,72] zinc, magnesium, calcium, barium, strontium, sodium, potassium, rubidium and lithium aluminates;[21,22,27,33,52,69] Nb_2O_5;[45] various spinels;[12,25,27,32,64] $CaCO_3$;[73] MgO;[26,66,72] zeolites;[66] diatomite;[12,13] carbon [37,51,66] and polymeric supports;[4,49] zinc titanate;[22,33] potassium silicate;[16] zinc,[25] cerium [53] and thorium oxides;[53] barium sulfate;[74] mixtures of metal oxides,[22,27,33,51,70] and fibre-glass materials.[28,55]

The catalytic properties of supported metals can be improved by promoters or additives,[4] which belong either to the catalytic system (promoters) or to the reaction mixture (additives). Metals, some non-metals, metal oxides, alkali and alkaline earth salts and hydroxides can function as promoters.

Among metal promoters, mention should be made of Zn,[12,27,28,60,72] Al,[11,28] Mo,[12,21,28] Ti,[28,40] Zr,[12,21,28] Ge,[12] Bi,[12,21] Sc,[12] In,[22,60] Pb,[12,20,21,40,53,64] Ga,[22,60] Cd and Ag,[53] Te,[40] and a group of lanthanides (La, Ce, Nd, Pm, Eu and Y),[12,28] and oxides of some 3d metals. Thus the introduction of titanium, niobium and cerium oxides increases the activity and selectivity of the Pd/SiO_2 catalytic system in acetylene hydrogenation and simultaneously suppresses sintering processes of disperse palladium particles, thus increasing the catalyst lifetime.[19,38,40]

A separate group of promoters comprises alkali (Li, Na, K, Rb, Cs) and alkaline earth (Be, Mg, Ca, Sr, Ba, Ra) metal derivatives, in particular, hydroxides and salts (hydrogencarbonates, carbonates, nitrates, hydrogensulfates, fluorides and iodides).[12,15,21,27,28,33,40,70] Alkali metal fluorides are complex promoters, because both the fluoride ion and the metal ion perform the promoting function. Some promoters are known in which alkali metal and fluorine atoms are parts of complex salts XYF_n (X is an alkali metal; Y is an element selected from the group Sb, P, B, Al, Ge, In, Tl and As; n is the number of F atoms in the YF_n^-) anion. In some cases, hydrofluoric acid or ammonium fluoride is used to introduce a fluorine compound into a catalyst.[32]

Among non-metals that promote the catalysts of alkyne and alkadiene hydrogenation, note sulfur,[28,32,66] phosphorus,[32] silicon [40,65] and boron;[75] sulfur and phosphorus can be present in the catalytic systems both as elements and as compounds such as potassium, sodium and ammonium phosphates or hydrogen- and dihydrogenphosphates; potassium, sodium and ammonium sulfates and their combina-

† J Osswald, K Kovnir, M Armbrüster, R Giedigkeit, R E Jentoft, U Wild, Y Grin, R Schlögl *J. Catal.* **258** 219 (2008).

tions.[32] A special place among the non-metal promoters belongs to fluorine,[11, 32, 51, 70, 72] although other halogens have also been mentioned.[10, 33, 70]

Examples of using additives that affect the performance of hydrogenation catalysts are few. Most often, gaseous CO present in the cracking gas is used for this purpose;[11, 23, 27, 31, 50, 51, 60] in this case, cracking gas is routed to hydrogenation without preliminary fractionation (so-called hydrogenation of the head fraction).[24, 25, 36, 60] The key benefits of the use of CO are noticeable increase in the selectivity of hydrogenation of the alkyne and diene impurities in olefin streams and simultaneous suppression of side reactions, namely, exhaustive hydrogenation and oligomerization.[24, 25, 28, 36, 50, 60, 76]

The selectivity of Pd/Al_2O_3-catalyzed liquid-phase hydrogenation of acetylene in the ethylene stream increases upon the addition of amines (n-butyl-, ethyl-, diethyl- and triethylamines, piperidine, morpholine, piperazine, ethylenediamine, triethylenediamine and ethanolamine).[14] A similar effect is observed in the selective hydrogenation of buta-1,3-diene to but-1-ene on Cu/SiO_2 in the presence of n-butylamine.[38] One can also suggest that amines, being sorbed on the Lewis and Brønsted acid sites of supports like alumina and aluminosilicates, would suppress their catalytic action towards oligomerization reactions.

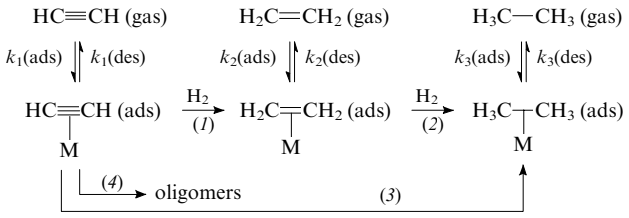
The poisoning action of sulfur compounds such as H_2S, COS, CS_2, thiols, thiophenols, sulfides and polysulfides on the catalyst of hydrogenation of acetylene and other unsaturated compounds is common knowledge.[31, 51, 77] Sulfur decreases the catalyst activity but increases the selectivity by blocking the most active reaction sites of the catalyst and thus suppressing the undesirable ethylene hydrogenation and carbon deposition on the catalyst surface.[4] Since catalysts of acetylene hydrogenation with low sensitivity to the poisoning effect of sulfur compounds have now been developed, the latter can be used as additives to reaction systems to suppress carbonization of the catalyst surface and increase the selectivity of hydrogenation with respect to alkenes. Examples of such catalytic systems are oxides or sulfides of zinc, gallium, copper, cadmium, chromium, molybdenum, tungsten, cobalt, nickel, ruthenium, iron or their mixtures[78] and Pd/Al_2O_3, Pd/TiO_2 and Pd/ZrO_2 promoted by alkali metal hydroxides, hydrogencarbonates, carbonates, nitrates, hydrogensulfates and fluorides, HF and NH_4F.[51]

Among the above-listed catalytic systems, Pd-containing supported catalysts are most active, most selective with respect to the target alkene and most durable. As a consequence, it is to these catalysts that the majority of publications on the mechanism of catalytic action, the effect of promoters and additives, the effect of structure and morphology of catalytic systems on their activity, selectivity and stability are devoted (see review[42] and references cited therein). Therefore, analysis of the modern views on the mechanism of heterogeneous catalytic hydrogenation of acetylenes and dienes is mainly based on the available data on functioning of Pd-containing catalysts.

III. Selective hydrogenation of acetylene

According to the existing views, hydrogenation of acetylene and its homologues can be described by Scheme 1.[4, 8, 42]

Scheme 1

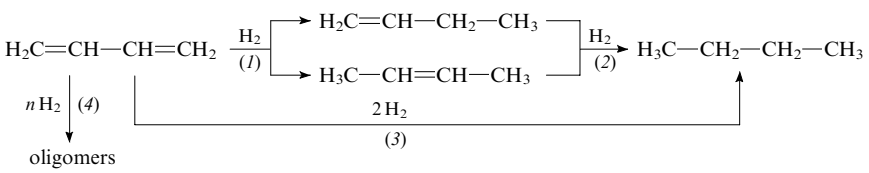


Successive hydrogenation of 1,3-alkadienes occurs in a similar way (Scheme 2).[4]

In the development of highly effective catalytic systems for purification of alkene-containing reaction streams from alkynes and dienes, it is necessary to find a compromise between two opposite requirements. On the one hand, the catalyst must be highly active in the hydrogenation of acetylene and diene impurities (the degree of acetylene or diene conversion should exceed 99%),[17, 18] which is dictated by stringent standards for their content in the reactor effluent (1 – 5 ppm); on the other hand, the catalyst activity must be moderate to prevent the undesirable hydrogenation of the target alkenes. The task of complete removal of these impurities from the reaction streams is complicated by high content of the alkene to be purified in these streams. The undesirable hydrogenation of the alkene not only means its loss but also produces a risk of uncontrolled exothermic reaction resulting in avalanche-like increase in the reaction temperature and exhaustive hydrogenation.[25, 42, 60, 77] Thus, a catalyst for selective hydrogenation of acetylene and its homologues should possess a thoroughly selected set of chemical, sorption and texture properties ensuring the highest reaction rate (*1*) and minimizing as much as possible the rates of side reactions (*2*), (*3*) and (*4*) (see Scheme 1).

A good point is that Pd-containing catalysts are more favourable for the major reaction (*1*) than for the side reaction (*2*) (this is confirmed by higher adsorption coefficients of alkynes compared to the corresponding alkenes[79, 80]). Under conditions of sorption equilibria, alkyne hydrogenation into alkene would dominate over hydrogenation of alkene into alkane virtually over the whole range of alkyne conversions. In addition, higher sorption affinity of the alkyne to Pd compared to that of alkene entails fast alkene desorption from the Pd surface at the instant of formation and prevents side reaction (*2*) with this alkene.[81] Actually, Pd catalysts showed a monotonic decrease in the selectivity to alkene depending on alkyne conversion.[40, 54, 61] Nevertheless, the substantial contribution of the sorption factor to the rate and selectivity of alkyne hydrogenation is confirmed by the difference in the behaviour of alkynes, alkadienes and alkenes in the com-

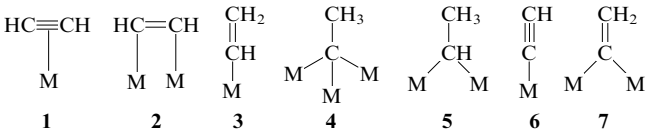
Scheme 2



petitive and separate hydrogenation. Indeed, in alkene + alkyne + alkadiene mixtures, alkynes and alkadienes show much higher reactivity than alkenes,[38, 40, 46] whereas in the case of separate hydrogenation, alkenes react faster.[81]

Recent studies have shown that the selectivity of Pd catalysts with respect to alkene cannot be interpreted without detailed consideration of the whole diversity of reaction sites and their behaviour under hydrogenation conditions. In this connection, noteworthy is the fact that ethylene is hydrogenated on Pd catalysts at high acetylene partial pressures,[82, 83] indicating the existence of a small group of reaction sites responsible mainly for ethylene hydrogenation on the catalyst surface. However, experiments with ^{14}C-labelled carbon demonstrated the existence of a direct route for acetylene conversion into ethane.[83, 84] In Scheme 1 this route is shown as generalized reaction (*3*). The sequence of reactions (*1*) and (*2*) represents hydrogenation of adsorbed acetylene to ethylene accompanied by ethylene desorption and readsorption followed by hydrogenation to ethane.[50, 54] Finally, generalized reaction (*4*) is oligomerization of acetylene, which occurs in parallel with the formation of ethylene and ethane.[85]

The results of systematic research into the evolution of the catalytic surface by means of advanced instruments and into kinetics of alkyne hydrogenation [76, 84, 86–91] resulted in the postulation of a number of adsorbed species that act as intermediates (or witnesses) in the surface reactions of acetylene hydrogenation. A detailed analysis of the studies dealing with the change in the Pd catalyst surface during acetylene hydrogenation has been reported in a review.[42]

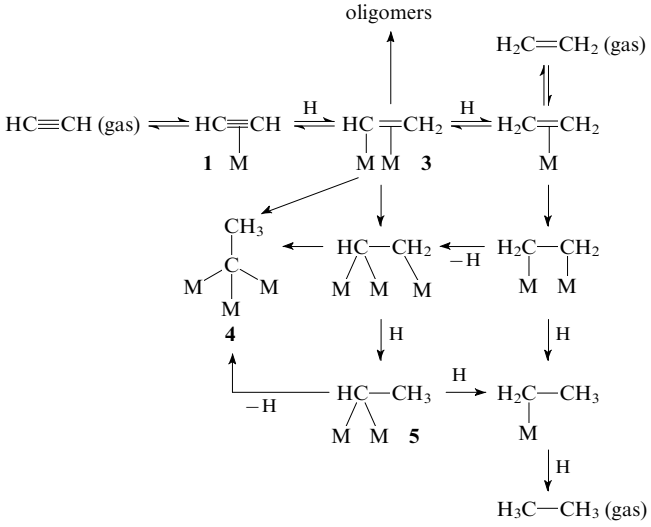


M is catalyst surface.

In particular, it is assumed that the acetylene primarily adsorbed as π-complex (**1**) is converted into acetylene (**2**) associatively chemisorbed (di-σ-adsorbed) on the catalyst surface. After addition of one H atom, chemisorbed acetylene (**2**) is converted into vinyl (σ-adsorbed) surface intermediate (**3**), which is considered to be the key species in the partial hydrogenation of acetylene to ethylene.[54] Surface-bound ethylidene (**5**) is interpreted as an intermediate of hydrogenation of vinyl species **3** to ethane,[54] while dissociatively adsorbed acetylene (**6**) and vinylidene (**7**) are involved in oligomerization and cyclotrimerization reactions, respectively.[4, 92]

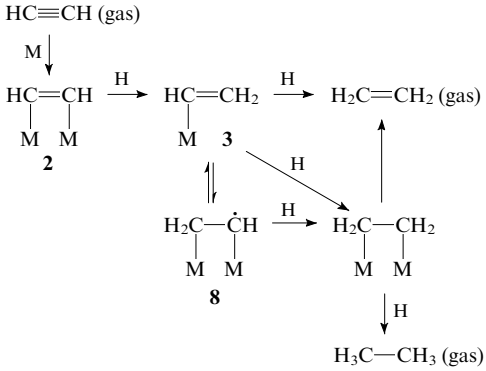
The fact of formation of species **2**, **4** and **6** under acetylene hydrogenation conditions was confirmed by Fourier transform infrared (FTIR) spectroscopy, sum frequency generation (SFD) technique and using isotope (D) labelling.[4] Angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) showed the formation of vinylacetylene and buta-1,3-diene, probably from vinylidene surface intermediates **7** or from chemisorbed acetylene **2**. In high vacuum, the formation of benzene as a side branch in the oligomerization route was detected [reaction (*4*)].[92] Taking into account these data, Molnár *et al.*[4] proposed a multiroute scheme for the formation of all possible products except for arenes (Scheme 3).

Scheme 3



There is also an alternative scheme for acetylene hydrogenation in which the key function is allocated to two surface intermediates, already mentioned vinyl compound **3** and free radical species **8** (Scheme 4).[4, 8]

Scheme 4



According to this interpretation, reaction selectivity is determined by competition of ethylene and ethane formation processes from these key intermediates. Free radical species **8** is also responsible for acetylene polymerization.

When comparing Schemes 3 and 4, note their common feature: in both cases, side reactions proceed through intermediates of higher multiplicity than the target reaction. Both schemes are used to interpret the effects of various factors (nature of the surface hydrogen species, character of the change in the reaction sites under the action of co-catalysts, promoters and additives, and dispersity of catalyst species) on the activity, selective action and durability of catalytic systems. Now we consider the action of these factors in more detail.

IV. Effect of various factors on the rate and selectivity of alkyne hydrogenation

1. Effect of hydrogen and its surface forms

Data on the catalytic hydrogenation of acetylene on Pd catalysts attest to participation of two hydrogen forms, namely, surface (adsorbed) and bulk (absorbed) hydrogen.[54, 93, 94] The former has higher selectivity in alkyne hydrogenation to alkenes, the reaction selectivity being dependent on its content and accessibility. An increase in the fraction of adsorbed hydrogen and a decrease in the

fraction of absorbed hydrogen in alkyne hydrogenation can serve as a tool for increasing the reaction selectivity to alkene.

Data on the selective hydrogenation of acetylene obtained in recent years open up interesting prospects for controlling the selectivity of this reaction. Studies of the hydrogen adsorption isotherms on the Pd catalyst surface, temperature-programmed reduction (TPR) of acetylene and temperature-programmed desorption (TPD) of ethylene demonstrated that by using bimetallic Pd–Ag catalyst, instead of neat Pd, it is possible to substantially decrease the bulk hydrogen concentration and increase the desorption temperature.[54]

Yet another possible way of affecting the selectivity of alkyne hydrogenation is the formation of subsurface carbon and surface Pd/C phase on Pd catalysts,[42] which were detected by X-ray photoelectron spectroscopy (XPS)‡ and high-resolution transmission electron microscopy (HRTEM) in early stages of hydrogenation.[34] These phases were shown to prevent transport of 'non-selective' hydrogen dissolved in the bulk towards the surface. This conclusion was confirmed experimentally by an increase in the selectivity of hydrogenation of pent-1-yne to pent-1-ene on $Pd/\theta\text{-}Al_2O_3$ with an increase in the content of subsurface carbon.

Shaihutdinov and co-workers[18] also pointed to participation of two forms of hydrogen in acetylene hydrogenation, in particular, that occurring in the surface region ('selective' hydrogen participating in acetylene hydrogenation to ethylene) and subsurface region (hydrogen responsible for exhaustive hydrogenation of acetylene to ethane). The increase in the fraction of 'selective' hydrogen in the surface region of the catalyst with the increase in temperature and the quantitative transition of all hydrogen into this form at 300 °C discovered by the authors are of particular interest. This finding accounts for the usually observed increase in the selectivity of acetylene hydrogenation to ethylene with temperature rise.[8]

However, in some cases, the selectivity to alkenes decreased with increase in temperature (see, for example, Refs 17 and 46), which indicates that the ratio of the two hydrogen forms and the efficiency of absorbed hydrogen spillover to the surface depend on the type of catalyst.

Another approach to increasing the selectivity of alkyne hydrogenation was proposed by Sellers and co-workers,[50] who postulated the presence of two reaction pathways differing in the hydrogenating agents occurring on the catalyst surface, namely, atomic and molecular hydrogen. Quantum chemical simulation was undertaken to give a quantitative substantiation for the change in the key characteristics of the catalytic hydrogenation of acetylene: reaction rate, selectivity to ethylene, contribution of oligomerization, the role of self-accelerating exhaustive hydrogenation, and so on. The approach proposed is formalized, as it ignores the difference between the state of reactants and intermediates in different phases and the possibility of alternative reaction mechanisms. Nevertheless, the explanation of acceleration of acetylene hydrogenation to ethane by surface dissociation of hydrogen proposed by the authors seems convincing.

‡ D Teschner, Zs Révay, J Borsodi, M Hävecker, A Knop-Gericke, R Schlögl, D Milroy, S D Jackson, D Torres, P Sautet *Angew. Chem., Int. Ed.* **47** 9274 (2008); D Teschner, J Borsodi, A Wootsch, Zs Révay, M Hävecker, A Knop-Gericke, S D Jackson, R.Schlögl *Science* **320** 86 (2008).

2. Effect of the second metal in bimetallic catalytic systems

The selectivity of alkyne hydrogenation on palladium or other Group VIII metals can be increased by introducing a second metal that also has catalytic activity. The effect of the second metal and other promoters on the efficiency of hydrogenation is due to their effect on the geometric and/or electronic properties of the catalyst active sites.[95] The geometric factor implies the change in the number of polyatomic active sites (assemblies) on the catalyst surface upon replacement of atoms of the major metal by atoms of the other metal. The displacement of some atoms of the major metal from the catalyst surface by atoms of the other metal decreases the hydrogenation rate and increases the selectivity. This was pointed out by Leviness *et al.*,[76] who studied the effect of copper on the selectivity of Pd–Cu-catalyzed acetylene hydrogenation. In addition, it was noted that a decrease in the number of polyatomic active sites consisting of atoms of the major metal results in a decrease in the probability of side oligomerization and exhaustive hydrogenation reactions due to the decrease in the number of multiply sorbed intermediates (see Scheme 3). This conclusion was drawn by Guczi *et al.*,[96] who studied hydrogenation of phenylacetylene on a Pd–Cu alloy. A decrease in the catalyst activity was attributed to dilution of the surface palladium atoms by copper atoms and the enhancement of the reaction selectivity, to the decrease in the average size of the active sites.

An increase in the selectivity of the partial hydrogenation of alkynes and suppression of oligomerization were also observed with other bimetallic systems such as Pd–Ag,[38–40,46,47,50–60] Pd–Au,[46,55,60] Pd–Cr,[40,62] Pd–Sn,[28,53,55] Pd–Zn,[27,53] *etc*. A decrease in the fraction of multiply adsorbed species was also noted by other authors,[17] who found that on going from Pd/SiO_2 to $Pd–Ag/SiO_2$,, the fraction of CO molecules adsorbed in the linear form increased with respect to CO adsorbed in the bridging form.

It is known that the addition of Group IB elements to palladium usually leads to higher selectivity of acetylene hydrogenation to ethylene but does not always increase the catalyst activity. The activity of Pd–Ag systems on inorganic supports has been studied in most detail.[17,18,36,50,54,97,98] In particular, powder X-ray diffraction (XRD) analysis of a Pd–Ag catalyst supported on Al_2O_3 shows that a Pd–Ag alloy has formed on the Al_2O_3 surface.[54] The formation of a Pd–Ag alloy on the $Pd–Ag/Na^+$-β-zeolite surface was also reported by Huang and Lobo,[97] who studied the catalyst surface by TEM, EXAFS and FTIR techniques. Examination of the XANES spectra of Ag–Pd catalysts showed[54] that the addition of the second metal induces electron density shift from Ag to Pd atoms, as a result, ethylene and acetylene adsorption on the catalyst surface is deteriorated, the adsorption of ethylene being decreased to a greater extent than that of acetylene. It is energy that underlies this effect, which reflects the contribution of the electronic factor to the selectivity of acetylene hydrogenation and suppression of oligomerization.

As noted above, the introduction of silver atoms into a palladium catalyst decreases the amount of absorbed hydrogen.[54] Hydrogen dissolved in the bulk of the Pd–Ag catalyst is retained more firmly than that dissolved in the bulk of monometallic Pd; therefore, it is less prone to spillover.[54,99] Hydrogen dissolved in Pd–Ag hardly reaches the surface and does not participate in hydrogenation. In

this situation, hydrogenation would involve only the 'selective' hydrogen adsorbed on the catalyst surface, which accounts for high selectivity of acetylene hydrogenation to ethylene.

Both factors, namely, the decrease in the adsorption coefficients of organic reagents and hydrogenation involving the 'selective' adsorbed hydrogen, relate to energy. The action of these factors can easily be interpreted by Scheme 3. Indeed, the preferred formation of ethylene over ethane in the acetylene hydrogenation is a result of easier desorption of the surface ethylene compared to desorption of acetylene, giving rise to an increase in the surface fraction occupied by acetylene.

The contribution of oligomerization to the overall process decreases due to the decrease in the concentration of the π,σ-adsorbed vinyl occurring in equilibrium with π-adsorbed ethylene (see Scheme 3). The decrease in the concentration of the latter is caused by the decrease in the ability of Pd sites to form π-complexes. Since the order of the oligomerization reaction with respect to the vinyl surface intermediate is higher than the order of hydrogenation, a decrease in the intermediate concentration leads to a decrease in the contribution of oligomerization to the overall process.

As a rule, the introduction of the second metal not only increases the selectivity of the hydrogenation catalyst, but also increases the catalyst durability. Owing to suppression of oligomerization, the amount of oligomers that are adsorbed on active sites and block the catalytic action decreases, and this retards the catalyst poisoning. In addition, spreading of the active sites on the catalyst surface as a result of dilution of the surface atoms of the major metal by atoms of the second component decreases the probability of agglomeration of these sites and sintering of the catalyst.[95]

3. Effect of promoters

The approaches based on the action of electronic and geometric factors can be used to interpret the promoting action of metals, non-metals and compounds possessing no inherent activity on the active sites of the catalyst.

The promoting effect of alkali and alkaline earth metals manifested as an increase in the selectivity and enhancement of the stability of Pd catalysts and decrease in their sensitivity to sulfur compounds[15, 20, 21, 51] is attributed to electron transfer from the promoter metal to Pd. This results in a decrease in the alkyne and alkene adsorption,[63, 100, 101] sorption of alkenes being decreased to a greater extent, which is favourable for their replacement by alkyne on the surface.

Despite the repeatedly noted promoting action of the fluoride anion,[11, 32, 51, 70, 72] no data interpreting its influence on the selectivity of alkyne hydrogenation, suppression of oligomerization and increase in the catalyst resistance against poisoning by sulfur compounds have been reported.

Obviously, due to the high electronegativity of the fluoride anion, its coordination to the palladium site should result in the shift of electrons from palladium to fluorine and increase in the positive charge on the palladium atom. As a consequence, the sorption affinity of alkynes and alkenes to the catalytic surface would increase and the selectivity to alkenes would decrease. However, it seems that the fluoride anion should be considered not as an isolated species, but rather as a component of the ion pair in which a hard acid (H^+, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+} cations) is ionically bonded to the hard base (F^-).[102] Such ion pairs can occur in the local environment of the palladium sites and decrease to some extent the number and the size of the polyatomic active sites involved in the multiple binding of substrates on the catalyst surface, which would suppress oligomerization and alkane formation. In addition, the cationic components of these ion pairs would bind nucleophilic sulfur compounds and prevent their interaction with palladium sites. The most effective promoters are salts with the general formula XYF_n.[11]

Figures 1 and 2 present the results of hydrogenation of the mixture 1.28% C_2H_2 + 95.22% C_2H_4 + 3.5% C_1 using unpromoted and KF-, $KSbF_6$- and KPF_6-promoted $Pd-Ag/Al_2O_3$ catalysts (the data were obtained by the Phillips Petroleum company[11]). It can be seen from the presented data that introduction of KF decreases the catalyst selectivity to ethylene, which is consistent with the electron-withdrawing action of the fluoride anion on the Pd sites, whereas the introduction of small amounts of KPF_6 and $KSbF_6$ increases the selectivity of acetylene hydrogenation by 15%–20%. The action of $KSbF_6$ and KPF_6 is based on the coordination of the complex anions SbF_6^- and PF_6^- by the Pd sites. The salts KPF_6 and $KSbF_6$ are hard acid–soft base pairs, while the Pd site should be regarded as a soft acid;[102] therefore, the anions SbF_6^- and PF_6^- readily

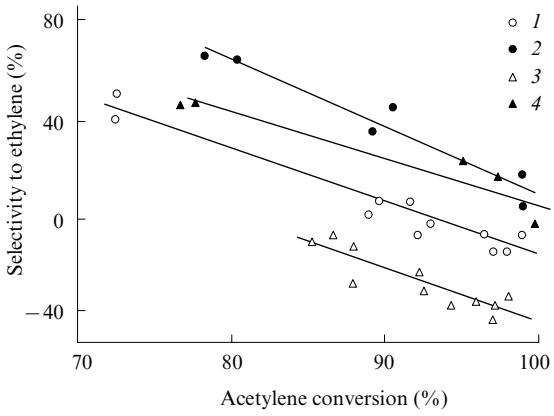


Figure 2. Temperature dependence of the selectivity of acetylene hydrogenation to ethylene on unpromoted (straight line *1*) and $KSbF_6$- (straight line *2*), KF- (straight line *3*) and KPF_6-promoted (straight line *4*) catalysts $Ag-Pd/Al_2O_3$ (from Ref. 11).
Reaction conditions: flow type setup, $H_2 : C_2H_2 = 2 : 1$.

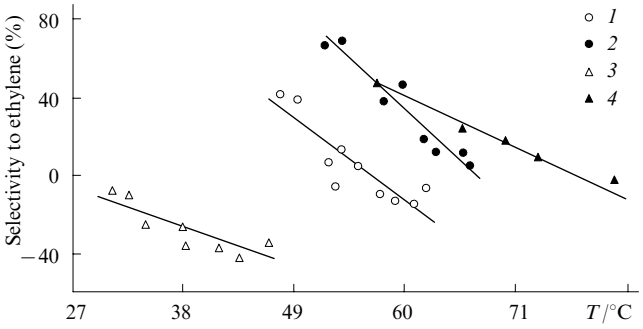


Figure 1. Acetylene hydrogenation on unpromoted (straight line *1*) and $KSbF_6$- (straight line *2*), KF- (straight line *3*) and KPF_6-promoted (straight line *4*) catalysts $Ag-Pd/Al_2O_3$ (from Ref. 11).
Reaction conditions: flow type setup, $H_2 : C_2H_2 = 2 : 1$.

leave their partner (K^+) and are coordinated to the Pd site. The newly formed $Pd-SbF_6^-$ and $Pd-PF_6^-$ bonds are rather strong; therefore, the ethylene molecules adsorbed on the catalyst surface are readily displaced from the reaction sites by these anions. This results in suppression of exhaustive hydrogenation reaction. Other complex salts, *e.g.*, KBF_4, $KAlF_4$, K_3InF_6, K_3GeF_6, $KTeF_6$ and $KAsF_6$, function apparently in a similar way.

Some elements that show superconducting behaviour and have no inherent catalytic activity in a pure state, also affect the palladium catalytic properties when alloyed with palladium. Thus the Pd–Si and Pd–Ge alloys show high selectivity in the partial hydrogenation of phenylacetylene, oct-1-yne [103] and hex-1-yne.[104] The high selectivity of the reaction to alkene was attributed to the geometric factor: dilution of the surface palladium atoms with silicon or SiO_2 results in a decrease in the probability of formation of the multiply sorbed ethylidyne and ethylidene surface intermediates, which decreases the probability of side reactions.[65]

The palladium–boron alloy is noticeably chemo- and stereoselective. A study of a Pd–B model system [95] has shown that boron blocks Pd sites and thus decreases the total number of active sites, mainly those participating in the multiple binding of organic molecules, which reduces the contribution of side reactions.

It has been noted that hydrogenation of acetylenes on Pd catalysts including binary catalysts gives rise to subsurface carbon and surface Pd/C phases, which prevent transport of 'non-selective' hydrogen dissolved in the bulk to the surface,[42, 77] but the formation of alloys in the case of binary catalysts results additionally in a decrease in the concentration (solubility) of 'non-selective' absorbed hydrogen.[93, 94] These factors together with the decrease in the number of active sites provide the general picture of the effect of promoters on the activity and selectivity of supported palladium catalysts.

The effect of lanthanide additives on the activity of Pd catalysts studied in relation to hydrogenation of but-1-yne was attributed [105] to the formation of intermetallic compounds Pd_3Ln (Ln = Ce, La, Sm, Pr, Nd). It was found that the stability of Pd_3Ln phases depends on the lanthanide nature. Thus the $LaPd_3$ and especially $CePd_3$ phases decompose on treatment with H_2, while $Pr(Nd,Sm)Pd_3$ do not decompose. High activity and low selectivity of but-1-yne hydrogenation on the palladium–cerium catalyst was rationalized as being due to partial decomposition of $CePd_3$ intermetallics to give active Pd sites. The remaining $CePd_3$ species surrounding the Pd sites act as electron acceptors giving rise to electron deficiency on the Pd atoms. The sorption affinity of alkenes to electron-deficient Pd atoms increases, which facilitates involvement of the latter in the secondary hydrogenation.

Palladium intermetallic compounds with Sm, Pr and Nd are fairly stable and have low activity in hydrogenation and high selectivity to alkene. This behaviour of Pd–Pr, Pd–Nd and Pd–Sm bimetallic catalysts was attributed to the electron transfer from the lanthanide to palladium. Excess electrons on the Pd atoms favour fast desorption of alkene from the catalyst surface. The compound $LaPd_3$ is intermediate in activity and selectivity between the two considered types of palladium intermetallics. Under the reaction conditions, this intermetallic compounds quantitatively decomposes and can be considered as a heterogeneous catalytic system $Pd_3-La_2O_3$; the behaviour of such catalyst is similar to the behaviour of palladium supported on pumice.[103]

Promoting of palladium catalysts of acetylene hydrogenation, Pd/SiO_2 and Pd/TiO_2, by transition metal oxides results in a marked increase in the reaction selectivity to ethylene and increase in the acetylene conversion.[19, 38, 40] It was shown that high stability of catalysts promoted by transition metal oxides is caused, first, by prevention of the catalyst sintering and, second, by a decrease in the coking of its surface. Kang *et al.* [19] used XPS to show that during reduction of Pd catalysts at 500 °C, Ce, Nb and Ti oxides are spread over the palladium surface and thus modify it. Having entered the local environment of the palladium sites, oxides prevent agglomeration of Pd species, suppress side reactions involving multiply adsorbed intermediates and facilitate ethylene desorption from the catalyst surface. This is confirmed by some other facts. In particular, the coverage of the SiO_2-supported palladium surface by Ce, Nb and Ti oxides is in line with the sequence of their effect on the selectivity: $Pd/SiO_2 < Pd-Ce/SiO_2 < Pd-Nb/SiO_2 < Pd-Ti/SiO_2$. It was also noted that the activity of promoted $Pd-Ti/SiO_2$ catalyst decreases to a much lesser extent after every regeneration cycle than that of the unpromoted catalyst.[40] These data agree with the less pronounced loss of the dispersity of the promoted catalyst during hydrogenation compared to unpromoted catalyst: according to X-ray diffraction data, in the case of Pd/SiO_2, the average size of Pd particles increased threefold (from 45 to 120 Å) during hydrogenation, while for $Pd-Ti/SiO_2$, the change was only 27% (from 48 to 61 Å).[38]

Analysis of the X-ray photoelectron spectra of unpromoted and metal oxide-promoted Pd/SiO_2 catalysts demonstrated a shift of the palladium peak in promoted Pd/SiO_2 towards lower energy. This shift was interpreted as being due to electron transfer from metal oxides to the palladium sites after partial reduction of the catalysts at 500 °C. Transition metal oxides function as electron donors with respect to the palladium sites. The increase in the electron density on Pd atoms naturally results in further decrease in its adsorption capacity for ethylene compared to that for acetylene [19] and thus increases the hydrogenation selectivity. The shift of the ethylene peak to lower temperature during the TPD [19] is direct evidence for this interpretation.

Recently it has been shown that the key role in the electronic effect of TiO_2 is played by Ti^{3+} ions.[39] The results of TPD studies attest to a decrease in the number of active sites of multicentre adsorption on the palladium surface under the action of oxide promoters.[19] This is caused by blocking of a part of surface palladium atoms by atoms of the promoter and is in line with the above presented XPS data and results of FTIR measurements of CO chemisorption,[19, 38] which demonstrated a decrease in the amount of multiply sorbed CO under the action of oxide promoters. A similar situation occurs with sorption of ethylene. The high-temperature peak (125 °C) identified in the TPD of ethylene,[40] which was attributed to di-σ-bonded ethylene responsible for the formation of ethane, was much less intense in the case of $Pd-Ti/SiO_2$ than in the case of unpromoted Pd/SiO_2. Thus, the decrease in the sorption ability of ethylene upon the addition of transition metal oxides caused by the effect of the electronic factor is supplemented by the geometric factor, specifically, suppression of the formation of multiply sorbed di-σ-bonded ethylene.

The decrease in the contribution of oligomerization upon the introduction of oxide promoters was confirmed by the data from thermogravimeteric analysis,[38] which demonstrated a decrease in the yield of so-called 'green oil' and in the average molecular weight of oligomers on going from Pd/SiO_2 to $Pd-Ti/SiO_2$. These results are in good agreement with a decrease in the deactivation rate of the titania-promoted Pd/SiO_2 catalyst and are attributable to a decrease in the fraction of Pd sites involved in multicoordination upon the addition of titania to Pd/SiO_2.[38]

Systematizing the data on the effect of various groups of promoters (Group IB metals, transition metal oxides, nonmetals) on the selectivity and stability of Pd catalysts supported on SiO_2 in acetylene hydrogenation, Moon and co-workers [38] chose the most effective representative of each group of promoters, namely, Ag, TiO_2 and Si, and showed that in terms of the above-mentioned characteristics, catalysts promoted by these elements are arranged in the following sequence: $Pd-Ag/SiO_2 > Pd-Ti/SiO_2 > Pd-Si/SiO_2$. It is pertinent to note that the effect of Ag is mainly related to the energy factor,[36] that of Si is due to the geometric factor [106] and that of TiO_2 to both.[40] Thus, $Pd-Ag/SiO_2$ is the catalyst of choice as regards the lifetime and selectivity, although as regards activity, it is inferior to TiO_2- and Si-promoted catalysts.

Currently, silver-modified Pd catalysts are most promising for hydrogenation reactions. Moreover, there is additional potential for improving these catalysts by doping them with alkali and alkaline earth metals, complex alkali metal salts XYF_n (Refs 11, 21, 27, 32 and 51) and lanthanides,[12] and by optimizing the texture and by distributing the active components and modifying agents over the catalyst core,[15, 22, 25–28, 52, 53] for improving the process characteristics by performing the process in the presence of CO [11, 24, 27, 78] and by pretreatment of the catalysts with oxygen compounds (CO, CO_2, NO and N_2O).[107, 108]

4. Effect of additives

The addition of nitrogen bases (quinoline, pyridine, piperidine, aliphatic amines, *etc.*) to the reaction medium results in blocking of the acid sites on the support surface and inhibition of oligomerization taking place on these sites. The point of view that takes into account the nucleophilic interaction of nitrogen-containing additives not only with the support, but also with active Pd sites having vacant d orbitals is more universal. This interaction weakens the palladium affinity to an alkene to a greater extent than to an alkyne,[38, 109, 110] which facilitates desorption of the alkene from the reaction sites and inhibits side hydrogenation reaction to saturated hydrocarbons. One more argument in favour of this interpretation of the promoting action of organic bases is the high selectivity of Pd catalysts supported on polyamides toward hydrogenation of highly unsaturated compounds.[111] In this case, each amide fragment of the polymer support acts as a nucleophile being coordinated to proximal Pd sites thus boosting their electron density and facilitating desorption of alkenes from these sites.

Being sorbed on the active sites of metals (Pd, Cu, *etc.*),[14, 38] nitrogen bases block the readsorption of alkene on the catalyst surface, whereas alkyne molecules readily replace amines in the Pd site, because Pd as a soft acid interacts weakly with amine, which is a hard base.[38, 102] This finally results in an increase in the selectivity to alkene. Alcohols [38] and sulfur compounds (hydrogen sulfide, organic sulfides, thiols, polysulfides, thiophene, *etc.*) behave in a similar way. The nucleophilic activity of sulfur compounds is determined, first of all, by high polarizability of the sulfur atom.[112]

Large sulfur-containing molecules block the catalyst active sites that multiply bind the alkyne molecules. The main effect from these additives is suppression of coke formation.[8, 77] In some cases, sulfur-containing modifying agents are deliberately added to hydrogenation catalysts (Ni, Cu, Pd); they decrease insignificantly the catalyst activity but considerably increase the selectivity and prevent coking.[8, 31, 66, 77, 78] Since some sulfur is lost during hydrogenation as a result of hydrogenolysis, make-up hydrogen sulfide is added to the reaction stream.[8]

Carbon monoxide is the best studied additive affecting the selectivity of alkyne hydrogenation.[11, 24, 27, 32, 60] Carbon monoxide possesses enhanced sorption affinity to the catalyst surface and thus behaves as a reversible poison. Due to higher sorption affinity compared to that of ethylene, CO actually displaces ethylene from the catalyst surface at the instant of formation and prevents the secondary hydrogenation. This point of view was confirmed by special experiments on deuteration of acetylene in the presence of CO.[113]

In most cases, the selective effect of CO in hydrogenation of acetylene is attributed to competitive adsorption of H_2, ethylene and CO. A point of principle in this interpretation is that the surface concentrations of hydrogen and ethylene decrease in the presence of CO.[114, 115] In the region of acetylene conversions of up to 90%, its content in the ethylene reaction stream is relatively high and it occupies a greater part of the surface. As conversion approaches 100%, the place of acetylene on the surface is occupied by CO, which prevents sorption of hydrogen and readsorption of ethylene and thus inhibits the secondary hydrogenation reaction of the sorbed hydrogen with alkene molecules.

Data on the effect of CO on the oligomerization are contradictory. In most cases (Ni, Pt, $Pd-Cu$ and $Pd-Ag$ catalysts), the yield of oligomers decreases with an increase in the CO pressure;[16, 24, 27, 76] however, in some cases, the formation of oligomers proves to be insensitive to the CO pressure [4] and even the degree of catalyst surface carbonization increases with an increase in P_{CO}.[116] This contradiction can easily be resolved. Since the reaction of oligomer formation has at least the second order with respect to the vinyl intermediate (see Scheme 3) and hydrogenation of this intermediate has the first order, the concentration of the intermediate is expected to decrease with an increase in the CO pressure, and hence the oligomerization rate may decrease. However, larger P_{CO} also leads to a decrease in the concentration of the surface hydrogen, which participates in hydrogenation, *i.e.*, to a decrease in the hydrogenation rate. Thus, the rates of competing oligomerization and hydrogenation reactions are equalized.

It should be borne in mind that sorption of hydrogen is less sensitive to CO pressure because the small size allows the hydrogen atom to be sorbed on a virtually occupied surface,[117] whereas suppression of oligomerization by blocking the multiple catalyst sites by carbon monoxide is most pronounced at high partial pressures of CO.

V. Problem of organization of kinetically controlled hydrogenation process and routes to its solution

Analysis of the available data on the selective hydrogenation of highly unsaturated compounds in hydrocarbon streams shows that high selectivity and durable catalyst operation are largely determined by accurate control of the temperature conditions of the process.[26] This can be attained by performing the reaction under kinetically controlled conditions where fast mass transfer ensures removal of temperature perturbations caused by high exothermicity of hydrogenation.[62] This problem is unique because the rate of the major alkene formation reaction should be 2–3 orders of magnitude higher than the rates of exhaustive hydrogenation and oligomerization side reactions.

Switching of the process to the uncontrolled diffusion regime would affect first of all the rate of the major reaction. In this case, the ratio of the rates of the major (diffusion-controlled) and side (chemical reaction rate-controlled) reactions would decrease and, hence, the selectivity of hydrogenation to alkene would become lower. In the diffusion-controlled process, the reaction sites conducting the major reaction would be susceptible to local overheating. These overheatings would also spread to the sites responsible for side reactions, which would lead to avalanche acceleration of the latter. Apart from the direct loss in selectivity, development of these processes would result in carbonization of the catalyst surface and finally in catalyst deactivation.[28, 29, 34, 35]

The possibility of the diffusion control depends to a large extent on the catalyst texture.[22, 95] The presence of micropores in the catalyst grains induces slow Knudsen diffusion and switching of the reaction into the internal-diffusion pore region. This results in coke formation in the micropores and deactivation of a considerable portion of the catalyst surface;[29] therefore, catalyst grains should contain mainly macro- and mesopores in which the transport of reactants and products through Knudsen diffusion is ruled out. The synthesis of such catalysts has been described in a number of patents (see, for example, patents [20, 26, 28, 29]).

Yet another requirement imposed on hydrogenation catalysts is the optimal distribution of the active component over the catalyst grain surface, which would provide its maximum activity and inhibition of side reactions. Methods for the production of so-called Pd skin-catalysts have been developed. In these catalysts, the major active component, palladium, is concentrated in the outer skin of the grain, which is favoured by the presence of wide transport pores and mesopores.[15, 16, 27, 52, 64] The second component functioning as a promoter (most often Ag) can be distributed throughout the grain size. It is obvious that in these catalysts the Ag : Pd ratio responsible for the selective action of the catalyst would increase on moving away from the grain surface inside the pores. In view of the decrease in the catalyst activity with the increase in this ratio, one may expect that the rate of chemical reaction would be 'adjusted' to the decreasing rate of diffusion in such a way that the kinetic control would also be retained in the narrow pore region.

The next important solution aimed at maintenance of the kinetic control of the reaction over the whole catalyst surface is related to extension of the range between the lower temperature limit corresponding to almost quantitative binding of highly unsaturated impurities with selectivity being as high as possible and the upper limit where the kinetic control is lost and the avalanche development of oligomerization and exhaustive hydrogenation side reactions start.[16] Evidently, the greater the difference between these temperatures, the lower the probability that the process temperature would run beyond the upper limit as a result of local overheating and the higher the probability of maintenance of the kinetic control. It is known that the upper temperature limit can considerably be raised by promoting the catalyst with silver and other Group IB metals or lanthanides [12, 16] or by changing the conditions of catalyst preparation (*e.g.*, by treatment of the $Pd-Ag/Al_2O_3$ catalyst with efficient reducing agents such as alkali metal borohydrides, hydrazine, formaldehyde, formic acid, ascorbic acid, aluminium powder in neutral or alkaline medium [70]).

An important factor in the control of temperature conditions is the phase state of reaction systems. Whenever possible and economical, it is desirable to carry out hydrogenation in the liquid phase because the thermophysical properties of liquids § allow more effective withdrawal of the reaction heat. This approach is used in hydrogenation of high-molecular-weight hydrocarbon fractions ($>C_4$), mixtures of light (C_2, C_3) and heavy (gas oil, naphtha) fractions or in the hydrogenation in inert solvents [13, 14, 17, 23, 27, 60, 66] where maintenance of most of the reaction mixture in the liquid state does not require high pressure.

In the case of gas-phase processes taking place most often in the adiabatic mode, in order to avoid high temperature gradients and switching to uncontrolled diffusion regime, hydrogenation is carried out in multistage reactors where cooled reactants (usually hydrogen) are fed through a number of inlets between the stages.[14, 22, 24] Thus the overall process heat can be dispersed over a larger reaction volume and some of the heat can be removed by fresh portions of cool reactant. A similar expedient is also used in liquid-phase processes except that in this case, a cascade of reactors is employed.[23, 60, 66] Mild thermal conditions of hydrogenation are sometimes attained by using hydrogen diluted by inert gases (N_2, N_2+CO).[60, 66] This method is justified when hydrogenation is carried out for high-boiling alkynes like phenylacetylene, which are easily separated from exhaust gases.

The use of catalysts with substantial numbers of macro- and mesopores inevitably results in a decrease in their specific surface area and, hence, the production output of unit reaction volume. A substantial contribution to the production output is made by the external surface area of the catalyst. Therefore, to ensure the required capacity of the unit, a rather large catalyst volume and turbulent reaction stream are required. These requirements dictate the shape of catalyst grains, which ensures, on the one hand, relatively low hydraulic resistance, and, on the other hand, turbulent reaction stream. The traditionally used catalyst shapes, *i.e.*, beds, pellets and cylinders, do not always satisfy these requirements.[25, 28, 51] Catalyst particles as worms, gear-wheels or ribbons are more suitable.[12] In recent years, catalysts with honeycomb structure and fibre and mem-

§ Due to high heat capacity of liquids, the dependence of temperature rise on heat evolution is smoother and the upper temperature limit is reached with lower probability.[14, 60]

brane catalysts have been used more and more often (Refs 28, 118–120).

The choice of the support is of crucial importance for high production output, selectivity, mechanical strength and durability of the catalyst.[121] Among known supports, various modifications of alumina and silica proved to be most suitable. Note that the use of alumina brings about a number of problems. First, the presence of acid sites on the Al_2O_3 surface promotes the formation of oligomers and, hence, carbonization of the catalyst surface.[29] Second, alumina is unsuitable for hydrogenation of moisture-containing raw material, as it is destroyed under the action of water vapour.[64] Third, alumina is brittle and has relatively high density, which entails fast wear of reactors with stationary or fluidized catalyst beds.[69] These problems can be solved by converting alumina into zinc, calcium, magnesium or lithium aluminates, which are fairly strong, stable against moisture and have a low content of acidic sites.[32, 52, 69] Low-acidic forms of silica are devoid of these drawbacks. Silica is chemically inert (it is passive with respect to oligomerization), has excellent mechanical strength and low density and is used successfully in alkyne and alkadiene hydrogenation (see, for example, publications [17, 19–21, 26, 27]). Numerous examples of compositions of related compounds (oxides, aluminates, titanates, *etc.*) used as supports have been reported.[22, 27, 64, 66, 69, 70]

VI. Criteria for the selection of hydrogenation process parameters

Parameters of catalytic hydrogenation process (temperature, pressure, contact time, reaction stream space velocity, reactant ratio, *etc.*) should be optimized taking into account, in particular, the contributions of various factors to the cost of the process, which changes with the change of these factors.

Temperature. Higher temperature is known to be favourable for complete conversion of impurities in hydrocarbon streams. However, an increase in temperature also gives rise to side reactions of exhaustive hydrogenation and oligomerization and increases the risk for the reaction to switch to the diffusion region with uncontrolled temperature in which the fraction of side reactions will grow in an avalanche manner. Thus, selection of the optimal hydrogenation temperature corresponding to complete transformation of highly unsaturated impurities in the hydrocarbon stream and the minimum yield of by-products under controlled temperature conditions is a highly important task. Depending on the particular catalytic system and other factors, the optimal temperature of alkyne and diene hydrogenation may range from 40 to 200 °C.

Pressure. Higher pressure favours acceleration of gas-phase and liquid-phase hydrogenation and maintenance of the reaction mixture in the condensed state in the case of liquid-phase processes. If hydrogen-treated gaseous reaction stream is subject to further processing under elevated pressure, then the pressure of hydrogenation can be increased to accelerate the reaction and reduce the reactor size. The upper pressure limit is determined by increasing cost of compression. However, higher pressure also promotes oligomerization. The selection of the optimal pressure depends on the phase state of the system, type of catalyst and some other conditions. In practice, pressures from 0.1 to 15 MPa are used.

Contact time and space velocity of the reaction stream. Due to the crucial role of sorption in the selective hydrogenation of alkynes and dienes (side hydrogenation of the alkenes formed starts immediately after complete consumption of a highly unsaturated substrate), appropriate contact time is important. Usually the shortest time needed to attain almost complete binding of highly unsaturated substrate is selected. The contact time in the hydrogenation of highly unsaturated substrates depends on the type of catalyst and some other parameters and ranges from 0.1 s to several tens of seconds.

The space velocity of the reaction stream is related to the effective contact time as follows:

$$\tau = \frac{V_c}{W},$$

where τ is the contact time, V_c is the volume of the catalyst bed, W is the space velocity of the reaction stream. Since the contact time is a regulated value, it is necessary to maintain an accurate proportion between the catalyst volume and the space velocity of the stream.

Organization of the effective hydrodynamic mode for the removal of external-diffusion retardation requires high linear velocity of the reaction stream n, which is related to the space velocity as follows:

$$\frac{\pi D_v^2}{4} n = W,$$

where D_v is the reaction space diameter. It follows from this relation that at a specified value W, the high linear stream velocity can be provided by the small cross-section of the reaction volume $\pi D_v^2/4$, which would correspond to a small diameter of the reaction space. Since the catalyst volume is constant, the cross-section of the reaction space can be decreased by increasing the length (l) of the catalyst bed.

$$V_c = \frac{\pi D_v^2}{4} l.$$

This would inevitably result in an increase in the hydraulic resistance of the reactor and growth of energy expenditure for compression.

Thus, selection of the optimal velocity of the reaction stream is based on the compromise between mutually exclusive requirements of intensifying the hydrodynamic behaviour and saving the cost of compression. Usually, the space velocity of the reaction stream ranges from 100 to 50 000 h^{-1}. If the reaction mixture is mechanically stirred, the space velocity of the stream may be much lower, from 0.1 to 60 h^{-1}.

Hydrogen : alkyne molar ratio. An increase in the hydrogen : alkyne ratio favours quantitative binding of highly unsaturated impurities in hydrocarbon streams; therefore, it is necessary to use more hydrogen compared to the stoichiometric amount. Excess hydrogen also inhibits the formation of oligomer and carbonization of the catalyst. However, the amount of hydrogen should not be too high in order to avoid exhaustive hydrogenation. In addition, the use of high excess of hydrogen increases the cost of isolation of the target products. Thus, in each particular process, it is necessary to select a hydrogen : alkyne ratio that would ensure complete transformation of substrates with no unde-

sirable exhaustive hydrogenation reactions and would not increase the cost of isolation of alkenes from the reaction stream.¶ In practice, the optimal hydrogen : alkyne ratios vary from 1 : 1 to 20 : 1.

VII. Effect of the degree of dispersion of the supported metal on its activity and selectivity in alkyne and diene hydrogenation in hydrocarbon streams

The rate of a heterogeneous catalytic reaction is determined by the sum of the rates of microreactions on the single active sites of the catalyst. The number of these sites divided by the total number of metal atoms is the degree of dispersion of the catalyst.[95] As the size of the catalyst particles increases, the degree of dispersion decreases because the ratio of the number of surface metal atoms to the total number of atoms decreases.

The degree of dispersion of the catalyst can affect both its specific activity (turnover frequency) and selectivity. In the case of bulk metals and micron- and submicron-sized metal particles, this effect is negligible. Crucial changes occur on passing to nanometre-sized particles. In this case, a change in the degree of dispersion of the catalyst affects both the geometry (geometric factor) and the energy state (electronic factor) of the active site. Thus, we are faced with the size effect. Since this is highly important for heterogeneous catalysis as a whole and particularly for catalytic hydrogenation, consider the size effect in catalysis in more detail.

Below we present [121] Boudart's classification of catalytically active particles, which is now generally accepted.

Bulk metal ($\gg 10^4$ Å) ⟶
⟶ ultradispersed metal ($\sim 10^3$ Å) ⟶
⟶ metal nanoparticle ($\sim 10^2$ Å) ⟶
⟶ molecular cluster (10 Å) ⟶ atom.

The intermediate position occupied by nanoparticles on going from the bulk metal to a single atom predetermines the specific features of the physicochemical properties of nanoparticles. The electronic,[122, 123] structural,[124, 125] magnetic,[126, 127] optical [128, 129] and adsorption [130] properties of metal nanoparticles differ considerably from those of bulk metals.

A vivid example of the effect of particle size of the metal on the adsorption properties has been reported by Smirnov *et al.*,[130] who studied adsorption of alkanes and alkenes on alumina and on alumina-supported gold and nickel particles. It was found that immobilization of gold nanoparticles on Al_2O_3 results in an increase in the adsorption heats of higher alkanes and alkenes. Thus the gain of the adsorption heat (ΔQ) of n-alkanes (C_6-C_8) on a support with applied gold particles with an average diameter of 3 nm with respect to that for pure support is 23 – 24 kJ mol^{-1}. For oct-1-ene, the ΔQ value is even larger, 36 kJ mol^{-1}. As the average gold particle size increases, ΔQ decreases and the adsorption heats of alkanes and alkenes on the samples with ultradispersed metal particles (nickel and gold particles 30 – 50 nm in diameter) almost coincide with the adsorption heats on pure alumina. The difference between the adsorption heats of alkanes and alkenes on gold nanoparticles of different size is apparently attributable to the strong interaction of these hydrocarbons with coordinatively unsaturated electron-deficient metal sites located on the vertices and edges of nano-sized crystallites. The smaller the nanocluster size, the greater the fraction of these sites on its surface. Unfortunately, in the study cited, the adsorption heats of acetylene and its homologues were not measured; however, it is beyond doubt that the effect for them will be even more pronounced.

Segura *et al.*[131] studied the adsorption of C_2 and C_3 molecules with C≡C and C=C bonds on gold nanoparticles. Using DFT technique, they calculated the binding energies of these molecules to gold atoms [using various model gold nanoparticles: Au(111) crystallite surface, Au(nanowire), Au_{19} cluster] and to palladium atoms [Pd(111)] for comparison. It was concluded that only alkynes are bound to gold nanoparticles, while both alkynes and alkenes are bound to palladium. The same researchers studied hydrogenation of a propyne + propene mixture on the Au/CeO_2 catalyst with an average Au particle size of 4 nm (scatter 1 – 11 nm) and demonstrated that supported gold particles show exceptional selectivity to C≡C bond hydrogenation in alkyne + alkene mixtures.

The first attempts to establish the relationship between the catalyst activity and particle size were undertaken by Kobozev [132] almost 70 years ago and continued by Boreskov [133] and Boudart [134, 135] in the 1960 – 1970s. These works resulted in classification of catalytic reactions into two classes: structure-sensitive (catalyst activity depends on the size of its particles) and structure-insensitive (activity does not depend on the particle size) reactions. The subsequent studies of reactions carried out in the presence of traditional catalysts, metal nanoparticles (Pd, Pt, Rh, Ru, Ni), led researchers to the conclusion that hydrogenolysis, skeletal isomerization and oxidation are most often structure-sensitive reactions, while hydrogenation of alkenes or unsaturated aldehydes is structure-insensitive.[8, 136 – 140] (As shown below, the conclusion about structure insensitivity of hydrogenation of alkenes and, especially, alkynes is not quite justified.)

It has been noted above that the size effect is related to the electronic properties (electronic effect) and/or the geometry of the catalyst active sites, surface metal atoms with different coordination numbers (geometric or assembly effect).[118] Now we consider variation of the activity of Group VIII metals towards hydrogenation of hydrocarbons from the standpoint of these effects.

First, consider the experimental data suggesting the dependence of the activity of Group VIII metal nanoparticles in the hydrogenation of unsaturated substrates on the nanoparticle size.

Figure 3 shows the dependence of the turnover frequency (TOF) of the Pt/SiO_2 catalyst in the hydrogenation of 3,7-dimethylocta-2,6-dienal on the size of Pt particles immobilized on SiO_2.[140] It can be seen that as the metal particle size increases from 1 to 5 nm, the catalyst activity increases approximately 25-fold. A further change in the size of immobilized Pt particles from 5 to 30 nm barely affects the catalyst activity.

A similar dynamics was observed for the hydrogenation of but-1-yne on Pd/Al_2O_3, Pd/pumice and Pd/CeO_2 (Fig. 4).[141 – 143] It can be seen from the data presented in

¶ A significant effect of $H_2 : C_3H_4$ ratio on the selectivity of propyne hydrogenation was reported, in particular, by Kennedy *et al.*[121]

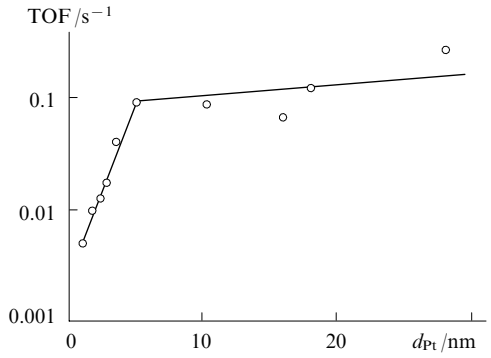


Figure 3. Turnover frequency (TOF) of the Pt/SiO_2 catalyst *vs.* platinum particle size (d_{Pt}) in hydrogenation of 3,7-dimethylocta-2,6-dienal (from Ref. 140).
Reaction conditions: $T = 373$ K, $P_{H_2} = 20$ atm, concentration of 3,7-dimethylocta-2,6-dienal: 1 mol litre^{-1}, hexane as solvent.

Fig. 4 that a decrease in the degree of dispersion (D) of Pd particles from 1 to 0.2 is accompanied by a 10–60-fold increase in the catalyst activity; however, upon further decrease in the degree of dispersion in the range from 0.2 to 0.02, the activity remains almost invariable.

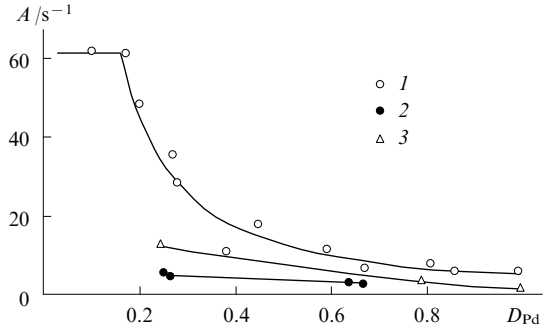


Figure 4. Activity (A) of Pd/Al_2O_3 (curve *1*), Pd/pumice (curve *2*) and Pd/CeO_2 (curve *3*) catalysts in but-1-yne hydrogenation *vs.* degree of dispersion (D) of palladium particles (from Refs 141–143).

The dependence of the Pd/Al_2O_3 catalyst activity in acetylene hydrogenation on the degree of dispersion of Pd particles has been reported by Gigola *et al.*[144] (Fig. 5). It can be seen that a decrease in the degree of dispersion of Pd particles from 0.8 to 0.1 brings about an approximately 10-fold increase in the catalyst activity. Unfortunately, the authors did not report the dynamics of variation of the catalyst activity following the change in the degree of dispersion for values of <0.1 or >0.8.[144] Nevertheless, this is not expected to differ much from the dynamics of activity variation of the Pd/Al_2O_3 catalyst in hydrogenation of but-1-yne (see Fig. 4).

The dependence of the Pd/C catalyst activity on the degree of dispersion of immobilized Pd particles for hydrogenation of 2,4-dinitrotoluene is shown in Fig. 6.[145] In this case, too, the activity was found to increase with a decrease in the degree of dispersion of the active component in the range from 0.4 to 0.02.

A comparison of the curves presented in Figs 4–6 demonstrates that the dynamics of variation of the catalyst activity as a function of the degree of dispersion of Pd

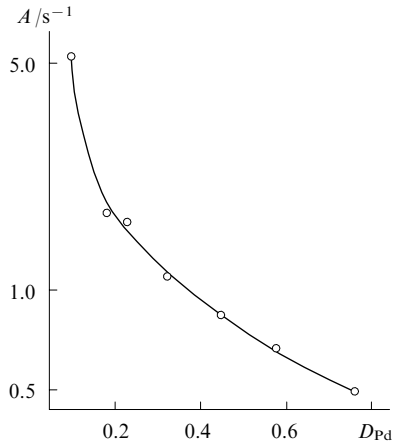


Figure 5. Activity of alumina-immobilized palladium particles in hydrogenation of acetylene *vs.* degree of dispersion of Pd particles (from Ref. 144).

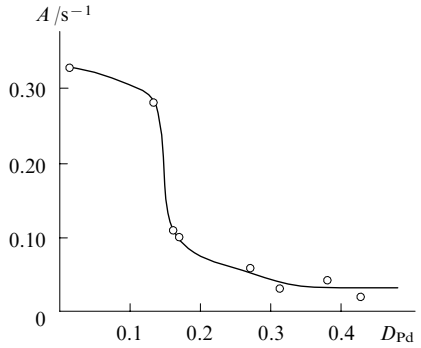


Figure 6. Activity of Pd/C catalyst in hydrogenation of 2,4-dinitrotoluene *vs.* degree of dispersion of palladium particles (from Ref. 145).

particles in the hydrogenation of various substrates depends little on the substrate nature. In all cases, as the degree of dispersion decreases (*i.e.*, size of immobilized particles increases) from 1.0 to 0.2, the activity increases, while further decrease in the degree of dispersion (below 0.2) barely affects catalyst activity in the hydrogenation. How can this trend be explained in terms of the electronic and geometric effects?

Consider the electronic effect. It is known that a decrease in the size of metal nanoparticles is accompanied by an increase in their electron deficiency,[146, 147] and, hence, Lewis acidity. The change in the electron density on the metal atom is known to be correlated with the binding energy (E_b) of the core electrons, which is determined experimentally from photoelectron spectra. It is known that a decrease in the Pd particle size from 6 to 1 nm entails an increase in E_bPd(3d5/2) by 1 eV.[148] Hence, the strength of adsorption of Lewis bases (including alkenes and especially alkynes) on the electron-deficient metal particles is expected to increase with an increase in the degree of dispersion. Adsorption experiments with the CO molecule isoelectronic to acetylene on $Pt/\gamma\text{-}Al_2O_3$ (Ref. 149) and Pt/MgO (Ref. 150) fully confirm this view. The authors of the cited studies[149, 150] found independently of each other that the intensity of the CO desorption peak on $Pt/\gamma\text{-}Al_2O_3$ and Pt/MgO sharply decreases with a decrease in the size of

platinum nanoparticles. Thus, the decrease in the activity of Group VIII metals in hydrogenation of alkenes or alkynes in the region of small nanoparticle sizes can be attributed to blocking of the work surface of the catalyst by chemisorbed molecules of the organic substrate.

The second factor affecting the decrease in the activity of hydrogenation catalysts in the case of small cluster sizes is competition between the adsorption of hydrogen and organic substrate. Naturally, alkenes and alkynes as stronger Lewis bases would be the first to be adsorbed, thus decreasing the concentration of hydrogen on the surface. Thus, the negative size effect (decrease in the activity with an increase in the degree of dispersion) in alkyne hydrogenation on palladium nanoclusters can be attributed to exceptionally strong adsorption of acetylene and other alkynes on the electron-deficient active sites. Apparently, the surface complexes thus formed are so stable that their destruction in the reaction with hydrogen proceeds with difficulty and is the rate-limiting step of the whole process.

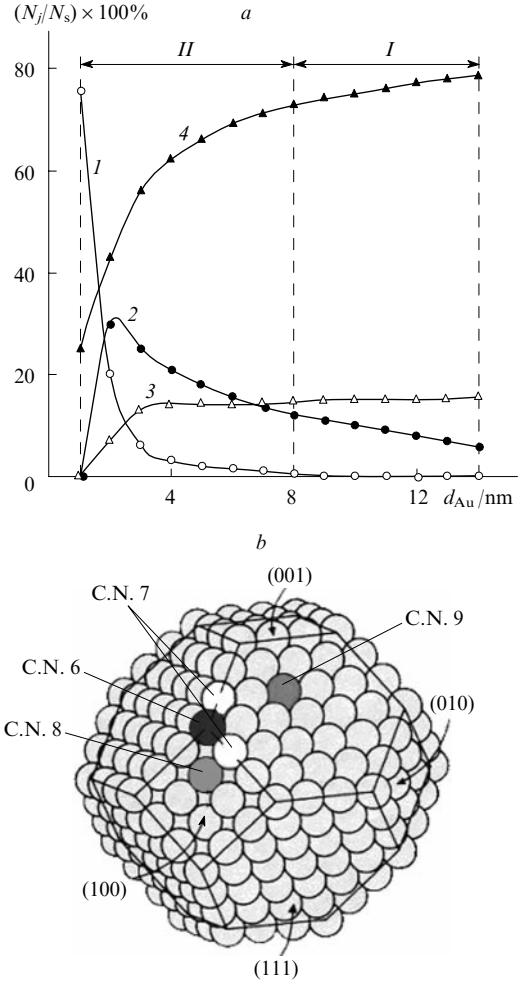


Figure 7. Relative concentrations of gold surface atoms N_j/N_s with coordination numbers of 6 (curve *1*), 7 (curve *2*), 8 (curve *3*) and 9 (curve *4*) *vs.* the diameter of gold nanoparticles d(Au) [(*a*) data of C Mohr, P Claus. *Sci. Progr.* **84** 311 (2001)]; the equilibrium cuboctahedral shape for Au particles was used in calculations (*b*) from Ref. 124).
N_j is the number of atoms with C.N. of j, N_s is the number of surface atoms.

The geometric factor acts in the same direction. This can be illustrated by Fig. 7. It can be seen that with a decrease in the particle diameter, the fraction of the corner (C.N. 6, curve *1*) and edge (C.N. 7, curve *2*) atoms for Group VIII metals increases non-monotonically, whereas the fraction of surface atoms with higher C.N. of 8 (curve *3*) and 9 (curve *4*) decreases. More detailed analysis allows one to identify region *I* (particles 8–14 nm in diameter) in which the total fraction of the corner and edge atoms almost does not change and region *II* (particles 8 to 1 nm in diameter) in which their fraction sharply increases from 12% to 75% of the total number of surface atoms. The chemisorption of alkenes and alkynes on palladium is much more efficient in region *II* than in region *I*, which is expressed as higher surface coverage for nanoparticles with diameters of 1–8 nm than for particles with diameters of >8 nm. As a consequence, Group VIII transition metal particles with sizes of >8 nm would be more active in hydrogenation than 1–8-nm particles. The data of Figs 3–6 are in good agreement with these conclusions. It is noteworthy that for particles with size of >8 nm, the surface geometry almost does not change, which is manifested as the observed invariable activity of these particles.

Apart from platinum and palladium, size effects were also studied for other Group VIII metals (Rh, Ru, Ni, Fe) (see Ref. 151 and references cited therein). It was concluded that on passing from 1-nm particles to 5–6-nm particles, the activity increases approximately 10–25-fold, while further change in the size of immobilized particles from 5–6 nm to 30–40 nm almost does not affect their activity in hydrogenation. The decrease in the activity of Group VIII metals with small particle size in the hydrogenation of alkenes or alkynes is caused, as noted above, by catalyst poisoning as a result of irreversible adsorption of organic substrate molecules. The invariable activity for 5–30-nm particles is due to almost equivalent nature of surface metal atoms.

Gold nanoclusters occupy a specific position among the metals studied.[131] Figures 8–12 show dependences of the activity of Au catalysts in the hydrogenation of some unsaturated hydrocarbons on the size of immobilized gold particles.[47, 152–154] It can be seen from Fig. 8 that the activity of <3-nm gold nanoclusters is low.[152] For these particle sizes, the size effect in the gold-catalyzed hydrogenation resembles that observed for other transition me-

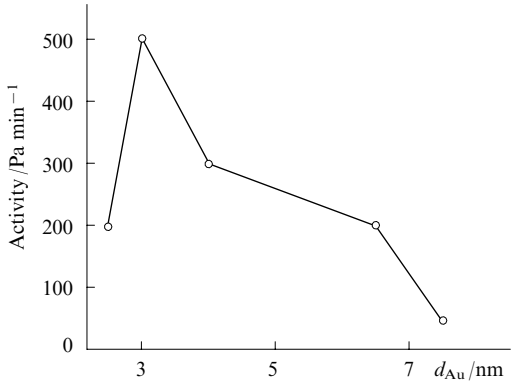


Figure 8. Activity of gold nanoparticles in acetylene hydrogenation at 523 K *vs.* size of Au particles immobilized on alumina.[152]

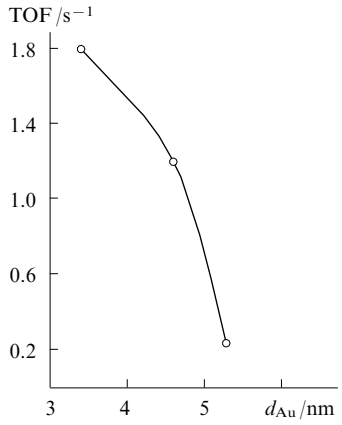


Figure 9. Turnover frequency of immobilized gold particles in hydrogenation of crotonaldehyde at 500 K *vs.* size of Au particles.[47]

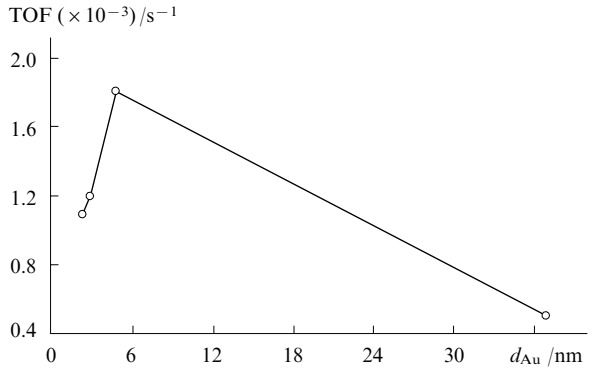


Figure 10. Turnover frequency of immobilized gold particles in hydrogenation of buta-1,3-diene at 423 K *vs.* Au particle size.[47]

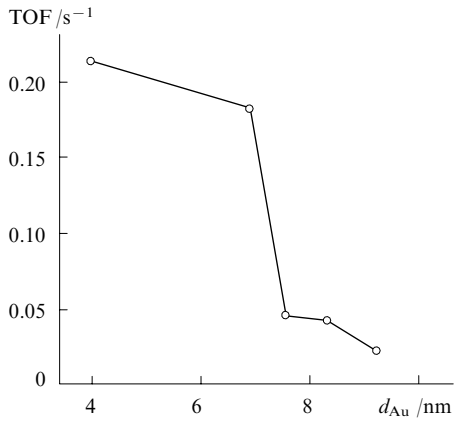


Figure 11. Turnover frequency of immobilized gold particles in hydrogenation of acrolein at 513 K *vs.* Au particle size.[153]

tals. However, as the size of gold particles is reduced from ~10 to 3 nm, the hydrogenation rate sharply increases.

This sensitivity of hydrogenation reactions to the size of nanoparticles of the metal catalyst in the range from 3 to 10 nm is observed only for gold nanoclusters. The differences between the behaviour of small gold particles and those of Pd, Rh or Ni were attributed to different types of

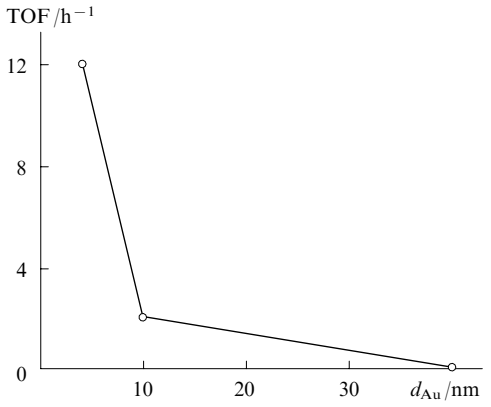


Figure 12. Turnover frequency of gold nanoclusters in hydrogenation of dodec-1-ene at 373 K *vs.* Au particle size.[154]

'roughnesses', *i.e.*, corners, edges and other surface areas containing metal atoms with low coordination numbers.

On Pd, Rh or Ni nanoclusters, irreversible chemisorption of unsaturated compounds takes place, which is accompanied by destruction and condensation processes, resulting in surface blocking and giving rise to seeds of carbonaceous deposits. In this case, if the roughness occupies a considerable portion of the surface, the activity and durability of the catalyst decrease. Relatively large clusters with developed flat faces on which hydrogenation takes place are the catalysts of choice. In the case of gold clusters, the situation is absolutely different: the Au atoms located on flat faces are insufficiently active, and it is the roughnesses that are the sites on which reversible adsorption and hydrogenation of hydrocarbons take place. The decrease in the size of gold nanoclusters from 10 to 3 nm is accompanied by a sharp increase in the number of these sites and, hence, increase in activity.

Generally, rather contradictory data on the effect of degree of dispersion of metal particles on the activity of hydrogenation catalysts may result from the fact that authors of the cited publications studied the catalytic activity of metal particles using different ranges of particle size. Some of them worked with particle sizes corresponding to the ascending branch in the curve of activity *vs.* degree of dispersion, while the other, with particles corresponding to the descending branch. Nevertheless, it seems reasonable that the decrease in the particle size and the increase in the particle electron deficiency would result in the increase in the adsorption of unsaturated compounds to such an extent that their subsequent transformations would be considerably retarded.[147,155]

Contrary to expectations, some data on alkyne hydrogenation (see, for example, Refs 141, 143, 148, 156–158) show that catalysts with low degree of dispersion have higher selectivity to alkenes than highly dispersed catalysts. However, in some other cases no noticeable effect of particle size on the selectivity was found.[159–162] Unexpectedly, 100% selectivity to ethylene with 100% conversion of acetylene was demonstrated by highly dispersed Au/Al_2O_3 catalyst.[152] In view of this fact, the behaviour of catalysts based on nano-sized gold calls for further research, first of all, as regards their stability and productivity.

It can be stated with regret that the role of size effects is least studied for bimetallic catalysts, which are promising for selective hydrogenation of alkynes. Meanwhile, com-

bined use of the specific properties of nano-sized catalysts, metal–metal synergistic effects, and the action of promoters and additives appears to be most promising approach to the perfection of selective hydrogenation processes of highly unsaturated hydrocarbons in alkene streams.

VIII. Conclusion

Hydrogenation of highly unsaturated impurities (dienes and alkynes) in hydrocarbon streams is an efficient method for purification of alkenes from these components. Extensive experimental knowledge has now been accumulated, which allows one to select hydrogenation conditions as to provide quantitative conversion of dienes and alkynes into alkenes with minimized hydrogenation of alkenes. However, the problem of simultaneous attainment of high activity, selectivity and durability of catalysts has not been completely solved. The search for new catalytic systems meeting these requirements and optimization of the process facilities for hydrogenation remain topical tasks. Supported nano-sized bimetallic catalysts based on palladium or gold are the catalysts of choice for selective hydrogenation of highly unsaturated impurities in hydrocarbon streams. A catalyst must be formed in such a way that all interactions taking place in the catalyst–substrate system (metal–metal, metal–promoter, catalyst–support, catalyst–reactants and so on) be directed to optimization of the whole process. This is a rather difficult but very challenging task, deserving obviously keen attention of specialists in catalysis and chemical engineers.

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