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Selective hydrogenation of unsaturated ketones and acetylene alcohols

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Contents

I. Introduction 923
II. Selective hydrogenation of unsaturated ketones 923
III. Selective hydrogenation of acetylene alcohols 929

Abstract. The data on selective hydrogenation of unsaturated ketones and acetylene alcohols are analysed. The requirements for choosing selective catalytic systems are surveyed. The routes for the reduction of oxygen-containing compounds and factors affecting them are considered. The bibliography includes 177 references.

I. Introduction

In recent years the problem of selectivity became one of the primary problems of catalysis. High selectivity is an essential characteristic of a catalyst, in addition to its activity and stability.[1,2] Selectivity is characterised by the ratio between the rate of accumulation of the target product and the overall rate of conversion of one of the starting compounds, by different routes, at a given temperature and a given composition of the reaction mixture.[3] A decrease in the selectivity of a catalyst results in the formation of side products that contaminate the target product. This leads to heavy expenses for its purification, to excessive consumption of raw materials and energy, and to deterioration of the environment owing to increase in the amounts of harmful aqueous and gaseous waste products.[4] The most significant and interesting in the theoretical and practical respects among the catalytic processes is catalytic hydrogenation, which is widely used for production of monomers, intermediate products, medical preparations, etc.

This review is devoted to the reduction of unsaturated ketones and acetylene alcohols of various structures and to choosing and developing selective catalytic systems.

II. Selective hydrogenation of unsaturated ketones

1. Hydrogenation of α, β-unsaturated ketones

The catalysts used for the reduction of double bonds in unsaturated ketones may be divided into two groups: the catalysts incorporating platinum metals as the main component or a modifier, and those containing Ni, Co, or Cu.

Hydrogenation of methyl vinyl ketone (MVK), benzylidenelacetone (BA), and benzylidenelacetophenone (BAP) selectively occurs in the presence of Rh/Al_2O_3, Pt and Pd oxides, colloidal Pt, Pd/C, Ru/C, Raney Ni, or Raney-type Co.[5–10] The ethylene bond, keto-group, and benzene ring are consecutively saturated in this process. It has been noted[7,11] that the order of the reaction of hydrogenation of C=C bonds in α, β-unsaturated ketones is close to zero. Enones having two or more substituents at the carbon atoms of the C=C bond have been shown to be reduced with low yields.[12]

As the temperature is increased, hydrogenation of BA slows down,[11] owing to pronounced adsorption of the substrate on the catalyst and displacement of hydrogen from the catalyst surface by benzylideneacetone. Introduction of halogen-containing additives to Ni-based catalysts also decelerates hydrogenation of BA, especially of its C=O group.

In order to ascertain the relationship between the reactivity of a series of unsaturated ketones (MVK, BA, and BAP taken as model compounds) and their chemical structure, the changes in thermodynamic functions: Gibbs free energy (ΔG°_{298}), enthalpy (ΔH°_{298}), and bond order ($p_{C=C}$) during hydrogenation have been calculated (without regard to effects of the solvent and the catalyst under standard conditions), and the results have been then compared with the rates of hydrogenation of these ketones on Raney nickel.[13,14]

The specific rates (W_{sp}) of hydrogenation of MVK, BA, and BAP in the presence of Raney nickel in ethanol and dioxane correlate with the values of ΔG°_{298} and $p_{C=C}$. This led the authors[13–15] to simple correlation equations:

$$W_{sp} = W_0' \exp(-K' \Delta G^\circ_{298}), \quad (1)$$
$$W_{sp} = W_0'' \exp(-K'' p_{C=C}).$$

Experimental data on hydrogenation of C=C bonds in unsaturated ketones are formally adequately described by the following equation:

$$W_i = \frac{k_i x_i}{1 + Q_i x_i}, \quad (2)$$

where W_i is the reaction rate when the initial concentrations of a substrate and a catalyst are equal to unity; k_i and Q_i are kinetic and adsorption parameters, $x_i = c_i/c_0$, where c_i is the concentration of the i-th component and c_0 is the initial concentration of the substrate. The need to take into account adsorption of MVK, BA, and BAP has been shown in specially carried out runs on hydrogenation of a mixture of ketones.[15]

The empirical equation (1) made it possible to predict the initial rates of the reduction of C_{13} and C_{18} ketones under standard conditions. Later, the results were confirmed experimentally. The deviation of the calculated values from the experimental results amounted to 15%.[16]

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Hydrogenation of mesityl oxide on Pt-based catalysts involves the reduction of either the C=C bond (40 °C) or both this bond and the keto-group depending on the conditions under which the process is conducted. Under mild conditions (atmospheric pressure of H_2, 25 °C) on Pd/C, only the C=C bond is hydrogenated.[17,18] In the presence of platinum boride, hydrogenation of mesityl oxide is less selective.[19]

Palladium-based catalysts (Pd/SiO_2, Pd/C, Pd black) also ensure selective formation of methyl isobutyl ketone in the gaseous or liquid phase (methanol, ethanol).[20-23] Highly selective reduction of C=C bonds in α,β-unsaturated ketones has been observed on Pd/C at moderate temperatures and hydrogen pressures (75 °C, 0.5 MPa).[24] Hydrogenation of mesityl oxide on Pd/Al_2O_3 occurs selectively at 40 °C (the yield of the hydrogenation product is 99 %).[23] Increasing the temperature to 210 °C results in the formation of methylisobutylcarbinol, i.e. the C=O group is reduced, as well as the double bonds. In addition, the product of dehydration of methylisobutylcarbinol, viz. 2-methylpentane, has also been detected. Dzhaparidze et al.[25] have studied the kinetics and mechanism of selective hydrogenation of mesityl oxide yielding methyl isobutyl ketone in the presence of the industrial Pd catalyst in the vapour phase in a flow-circulation system. They showed that all the experimental data are adequately described by the following equation

$$W = \frac{k_1 P_1 P_{H_2}^{1/2}}{P_{H_2}^{1/2} + k_2 P_1 + k_3 P_2^2}, \quad (3)$$

where P_1 and P_2 are partial pressures of mesityl oxide and methyl isobutyl ketone, k_1, k_2, and k_3 are constants. Based on the analysis of the data on the H/D-isotope exchange in mesityl oxide and methyl isobutyl ketone, a multistage mechanism involving the formation of a semihydrogenated form has been proposed for this process.[25]

For selective reduction of mesityl oxide, as for the hydrogenation of methyl vinyl ketone, Rh-based catalysts are used.[8,9,26] To increase the rate of the reaction, Rh, Pt, and Pd are modified with rare earth metals (Y, Er, Yb).[27,28] Nitrogen-containing Rh complexes[29] and Ru, Rh, and Pd complexes with phosphines[30] are active and selective in the hydrogenation of mesityl oxide and methyl vinyl ketone. Borunova et al.[29] compared the catalytic activities of Rh/C and of Rh complexes with *N*-phenylanthranilic acid and tyrosine in the hydrogenation of α,β-unsaturated ketones and found that the activity of homogeneous catalysts is considerably higher than that of the heterogeneous Rh/C catalysts.

Reduction of α,β-unsaturated ketones in the presence of Rh, Ru, Pd, or Pt deposited on carbon has been shown to involve both direct hydrogenation of the C=C bond and 1,4-addition of hydrogen to the enone system.[10,31]

A large number of publications[32-37] are devoted to hydrogenation of mesityl oxide catalysed by Ni. In the presence of Raney nickel in various solvents, both the C=C bond and the carbonyl group are hydrogenated,[38,39] i.e. the reduction occurs nonselectively. It was assumed that the reaction, which occurs on the catalyst surface, between chemisorbed atomic hydrogen and adsorbed or nonadsorbed substrate is the rate-determining step of the process.[38] When supported Ni catalysts (30% Ni/Al_2O_3, 160–196 °C, without a solvent) are used, a yield of methyl isobutyl ketone of more than 96% can be achieved.[37]

Modification of Ni catalysts with halides of Group I, II, and III metals results in the increased selectivity of the process with respect to the saturation of C=C bonds.[35,36,40] According to the results obtained by Zhabrova,[41] modification is considered as a general phenomenon, which involves both promoting and poisoning of a catalyst. The use of NiI_2, ZnI_2, CdI_2, $FeBr_2$, $CdBr_2$, and $CoCl_2$ as modifying additives for Raney nickel has been patented.[33] The yield of methyl isobutyl ketone reached 94%. The authors of a paper,[40] who have compared the results of hydrogenation of mesityl oxide in the presence of unpoisoned Raney Ni and of Raney Ni poisoned with KI, concluded that adsorption of mesityl oxide on the catalyst is weaker than that of H_2.

Experiments have shown that the shielded double bond in mesityl oxide is hydrogenated at the same rate as the terminal C=C bond in methyl vinyl ketone.[42] Absorption of 1 mole of H_2 at 42 °C and an atmospheric pressure of hydrogen affords the saturated ketone with high selectivity. When the pressure is increased to 6 MPa, the C=O group is also reduced, but the second mole of H_2 is absorbed very slowly. It has been shown that the isolated double bond in 2-methylpent-1-en-4-one is hydrogenated four times more slowly than the C=C bond in mesityl oxide.

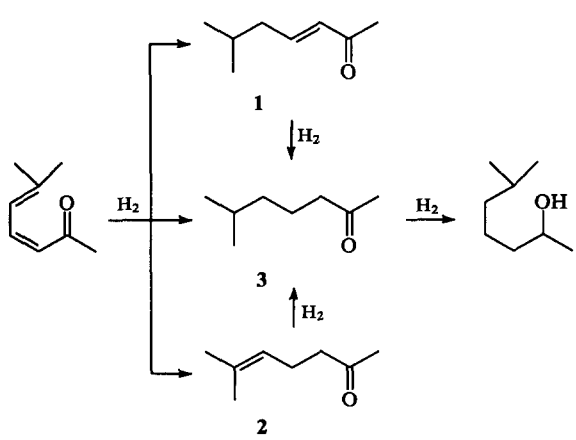
Hydrogenation of mesityl oxide in the presence of copper-based catalysts is not sufficiently selective.[43,44] The highest yield of methyl isobutyl ketone (86.5%) has been obtained at 180–220 °C, at a hydrogen : substrate molar ratio of approximately 1.2, in the presence of Cu_x-Cr_x-Mn oxides deposited directly on a carrier treated with a solution of H_2CrO_4. The process occurs more selectively in the presence of homogeneous catalysts: Cu compounds with additions of $LiAlH_4$.[45]

2. Hydrogenation of polyenones

When the conjugated system of unsaturated ketones is extended by one more double bond, hydrogenation products become more diverse. For example, reduction of 6-methylhepta-3,5-dien-2-one in hexane in the presence of $Pd/CaCO_3$ at atmospheric pressure of hydrogen and ambient temperature affords 67.6% of 6-methylhept-3-en-2-one and 30.2% of 6-methylheptan-2-one,[46] i.e. hydrogen adds initially at the C(5)=C(6) bond and then at the C(3)=C(4) bond. Hydrogenation of the diene alcohol on the same catalyst results in the initial saturation of the C(3)=C(4) bond. Apparently functional groups affect orientation of dienone molecules on the catalyst surface.

When dienones are hydrogenated in the presence of modified catalysts, hydrogen adds initially to the C(3)=C(4) bond and then to the C(5)=C(6) bond. A study[47] has been devoted to changes in the selectivity of the Pd-based catalyst occurring under the action of various modifying additives. Hydrogenation of 6-methylhepta-3,5-dien-2-one yields enones **1** and **2** and 6-methylheptan-2-one (**3**) (Scheme 1). To elucidate the route to the saturated ketone, hydrogenation was carried out in the presence of 5% $Pd/CaCO_3$, 1% Pd/Al_2O_3, or 1% Pd/TiO_2 at 1–5 MPa. In the case of unmodified Pd catalysts, the formation of ketone **3** is preceded by intermediate **1**. Modification of the catalysts with Cd promotes the preferential addition of H_2 to the C(3)=C(4) bond. Hydrogenation of 6-methylhepta-3,5-dien-2-one in the presence of Rh catalysts (Rh/Al_2O_3) with addition of 0.01%–1% Pb in methanol (70 °C, P_{H_2} = 5 MPa) or in the presence of Rh–Ru catalysts (2%–5% of the metal) deposited on carriers (Al, Ti, Zn, Zr, and Si oxides and aluminosilicate modified with 0.01%–1%

Scheme 1



Pb, Sn, Cd, or Bi[48]) affords enone **2** as the main product. In other words, as in the case of modified Pd catalysts, the C(3)=C(4) bond is the first to be saturated.

The route to the reduction of double bonds in a dienone system is determined not only by the nature of the catalyst and modifying agent and the number of these bonds, but also by the character of substituents in the dienone moiety. For example, in the case of cinnamylacetone in which the diene group is linked to an aryl group, the C(3)=C(4) bond is saturated first in the presence of Pd black, and then the saturation of the C(5)=C(6) bond takes place.[49]

Pseudoionone — 6,10-dimethylundeca-3,5,9-trien-2-one (A_1, a C_{13} unsaturated ketone), contains an isolated double bond in the 9,10 position, in addition to the dienone moiety. Several patents contain information on synthesis of hexahydropseudoionone — 6,10-dimethylundecan-2-one (A_4, a C_{13} saturated ketone) in the presence of 5% Pd/C, 5% $Pd/CaCO_3$, Pd/gauze, and Rh/gauze (50–70 °C, $P_{H_2} \leqslant 7$ MPa, yield 92.5%–96%).[50–53]

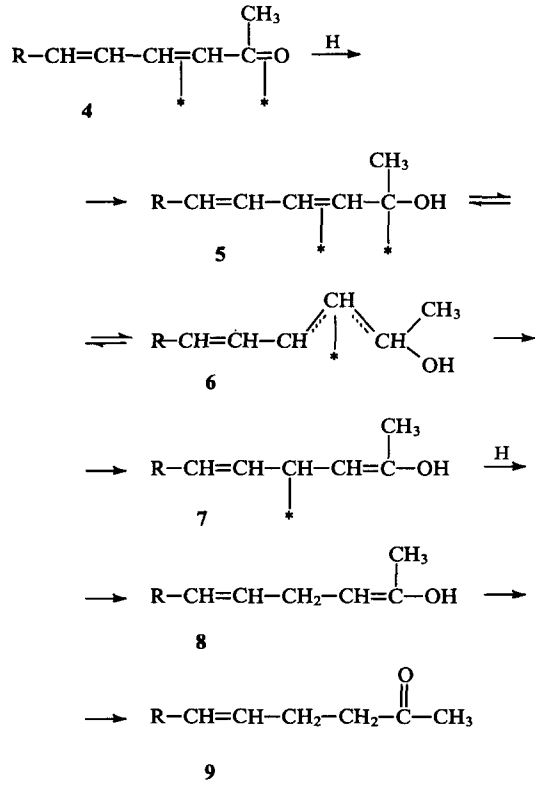
The liquid-phase hydrogenation of A_1 on 5% Pd/C has been found to yield products with various degrees of saturation: 3,4-dihydropseudoionone (*cis*- and *trans*-geranylacetone), 5,6-dihydropseudoionone (A_2), 3,4,5,6-tetrahydropseudoionone (A_3, citronellylacetone), and *cis*- and *trans*-isomers of 3,4,9,10-tetrahydropseudoionone.[54] Chromatographic analysis by the authors not only allowed them to detect these products in the reaction mixture but also confirmed that hydrogenation of ketone A_1 predominantly occurs via a multi-stage mechanism. Absorption of one mole of H_2 results in the formation of 70% of ketone A_2, and after absorption of two moles of H_2, 93% of ketone A_3 is produced.

In the hydrogenation of polyunsaturated and diene ketones in the presence of Ni[55] and Co catalysts,[56] as in the case of Pd catalysts,[46] H_2 adds mostly at the C(5)=C(6) double bond, and to a lesser degree it adds at the C(3)=C(4) bond. Modification of the Ni and Co catalysts with Pb, Cd, and Zn metals[48,49,55–59] or cations[60–62] changes the course of hydrogenation of this dienone: H_2 adds at the C(3)=C(4) bond conjugated with the keto-group. The catalysts used are Raney-type catalysts or blacks deposited on carriers (TiO_2, $Ca_3(PO_4)_2$, V_2O_5, ZnO, Al_2O_3, and MoO_3). Carriers affect the activity of catalysts without changing the reaction pathway.[57] Hydrogenation is carried out at temperatures of 20 to 125 °C and hydrogen pressures varying from atmospheric to 10.1 MPa; the amount of modifying additive is varied from 0.01% to 60% with respect to the weight of the catalyst. Modifiers not only affect the reaction pathway, but also lower activity of the catalyst and substantially decelerate hydrogenation of the carbonyl group.[49,59,62] The action of these additives cannot be reduced solely to poisoning the catalyst, they also promote it. Under severe conditions[59] the carbonyl group is reduced also on modified catalysts. Dienones (hepta-3,5-dien-2-one, 6-methylhepta-3,5-dien-2-one) and ketone A_1, the molecules of which contain diene groups, in the presence of both modified and unmodified catalysts behave in a similar way. This implies that the observed regularity is general: hydrogenation on catalysts modified with inorganic compounds begins with addition of hydrogen at the 3,4 positions. Introduction of pyridine leads to analogous results.[57]

It has been found that the structure of dienone influences the mode of addition of H_2.[59] For example, hydrogenation of hepta-3,5-dien-2-one and 6-methylhepta-3,5-dien-2-one in the presence of Ni catalyst modified with lead affords hept-3-en-2-one, hept-5-en-2-one, and 6-methylhept-5-en-2-one, respectively. Thus, in the latter case, hydrogen adds only at the C(3)=C(4) bond. This is probably due to the presence of a substituent at the C(6) atom and to a different orientation of the dienone molecule with respect to the surface of the catalyst.

Double bonds of a dienone are saturated either independently of each other or by 1,4-addition of hydrogen to the enone group. In fact, addition of hydrogen at the C(3)=C(4) bond, conjugated with the carbonyl group, may occur as the addition to the 1,4 positions of the enone system via intermediate formation of enol[60] (Scheme 2). In accordance with this Scheme, the final product, a ketone with a C(5)=C(6), is preceded by enol **8**, which is formed from the doubly-adsorbed substrate **4** via successive formation on the catalyst surface of semihydrogenated complex **5**, π-allylic complex **6**, σ-derivative **7**, and enol **8**. This Scheme has been confirmed by deuterium exchange. In the presence of the unmodified catalyst, enol is not produced.

Scheme 2



* is an active centre of the surface.

The results of these studies show that the change in the composition of the active catalyst surface caused by modification results in a change of its orienting properties and of the mechanism of the hydrogen addition to dienone.

A number of papers[16,63,64] present data on hydrogenation of pseudoionone under conditions excluding diffusion retardation. To increase selectivity of Ni catalysts the authors[63,64] used various modifying additives: K_2SO_4, KCl, KBr, and KI. It was found[63] that KI possesses the highest selectivity in the hydrogenation of the pseudoionone C=C bonds and all these modifiers, in terms of their selectivity, can be arranged in the sequence $K_2SO_4 < KCl < KBr \ll KI$.

When Zn and Cd halides were used, products of H_2 addition at the C(3)=C(4) bond of pseudoionone were detected in the catalysate. In the Fe^{2+}–Co^{2+}–Ni^{2+} series, the element with the greatest atomic number exhibits the highest catalytic activity.

The IR spectra of pseudoionone recorded after addition of $CoCl_2$ or $NiCl_2$ indicate that the additive interacts with the dienone system of the ketone: redistribution of the intensities of the absorption bands associated with the C=O group and the C=C–C=C bonds was observed.[16] Transition metal ions are likely to protect the ketone group against its reduction to an alcohol group.

To determine the optimum conditions for hydrogenation of the unsaturated ketone A_1 in the presence of the Ni–Co catalytic

system in isopropanol and to elucidate the reaction mechanism in detail, Sul'man[65,66] et al. investigated the kinetics of hydrogenation in a static system, varying the conditions of the process.

It was found that the reaction proceeds according to a parallel-sequential scheme [reactions (*1*)–(*4*), Scheme 3]. In addition to these reactions, transformation of the saturated ketone A_4 to the saturated alcohol A_5 ($A_4 \rightarrow A_5$) also occurs. The selectivity of hydrogenation of the C=C bonds in ketone A_1 diminished with increase in the temperature and hydrogen pressure. The highest selectivity with respect to ketone A_4 amounted to 95%–96%.

Hydrogenation of C_{13} and C_{18} polyene ketones in a dynamic regime in the presence of the Ni–Co catalytic system results in the accumulation of substantial amounts of saturated alcohols in the catalysate,[67] probably owing to retardation of internal diffusion.[68]

Hydrogenation of dienones is carried out not only on heterogeneous catalysts, but also in the presence of homogeneous catalysts, for example, Co complexes,[69,70] that are more selective in the formation of saturated ketones.

The saturation of polyenones in the presence of various catalysts may depend essentially on the initial concentration of the substrate and the nature of solvent. When the ketone concentration in the solution is increased from 10% to 50%, the reaction rate diminishes.[57] This can be attributed to adsorption of dienone from the catalyst surface with the displacement of hydrogen and to the complication of the process due to diffusion of hydrogen.

Experimental data on the kinetics of the hydrogenation of the ketone A_1 in Pr^iOH in the presence of 2% Pd/C are described by the linear relation[16,71–74]

$$\tau_{0.5} \sim q^n \quad (n = 1), \tag{4}$$

where $\tau_{0.5}$ is the time of half-conversion of ketone A_1 and $q = c_0/c_c$ (c_0 is the initial concentration of the substrate, c_c is the amount of the catalyst).

This relationship makes it possible to introduce the reduced time $\theta = t(c_c/c_0)$. Thus, the data obtained for different c_c values can be combined (Fig. 1).

To explain the experimental data, various kinetic models have been used.[75] Application of the equation

$$W_i = k_i x_i \tag{5}$$

for describing the kinetics of the consecutive conversion of ketone A_1 to the saturated ketone A_4 led to systematic deviations of the calculated results from the experimental data. This fact, together with the possibility of direct addition of two or three moles of H_2 to ketone A_1, required consideration of a parallel-sequential Scheme 3. It has been noted that in the consecutive conversion of ketone A_1 to A_4, the first mole of H_2 (according to chromatographic analysis) adds predominantly at the C(5)=C(6) bond of A_1 and to a slight extent at the C(3)=C(4) and C(9)=C(10) bonds. In addition, it has been shown in special experiments that the kinetic model should be constructed with due regard for adsorption of ketone A_3. Statistical analysis showed that the best results have been obtained by using Eqn (2) and parallel-sequential Scheme 3 [(reactions (*1*)–(*3*)] with due regard for the adsorption of ketone A_3. The curves calculated from Eqn (2) are in good agreement with experimental curves (see Fig. 1).

Hydrogenation of ketone A_1 in the presence of 5% Pd/C under dynamic conditions proceeded nonselectively with formation of the saturated alcohol. This is accounted for by the influence of the internal-diffusion retardation on the reduction of this ketone on Pd/C and by lyophilisation of the system when charcoal is used as the carrier.[76]

For hydrogenation of pseudoionone, ethanol[54,76] and methanol[53,57,59] have been used as solvents. In a study[16,64] of hydrogenation of ketone A_1 in the presence of the Ni–Co catalytic system, it was found that the selectivity of the process is

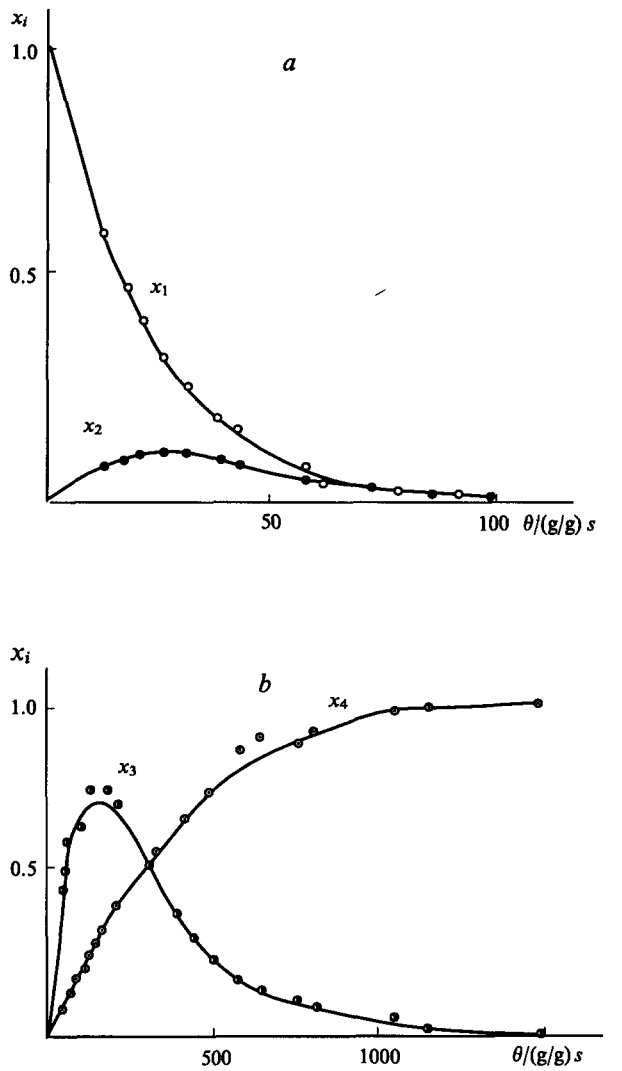
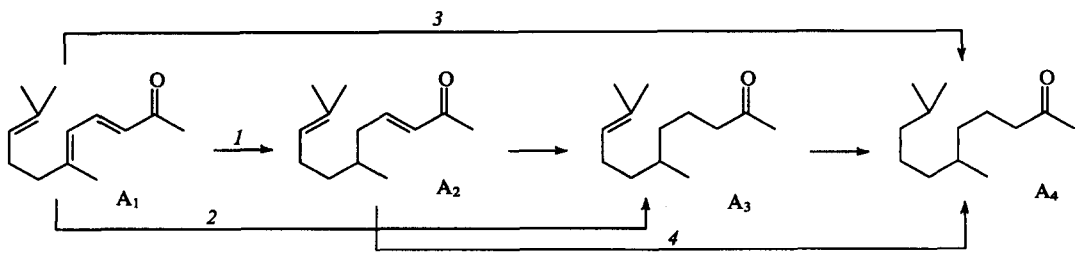


Figure 1. Composition of the catalysate in the hydrogenation of ketone A_1 in the presence of Pd/C ($T = 50\,^\circ C$, the hydrogen partial pressure is 2 MPa). Continuous lines show the results of the calculations; points correspond to experimental results.

Scheme 3



significantly affected by the nature of solvent (C_1-C_4 alcohols of normal and iso structures with addition of water were studied). In terms of the rate of the accumulation of ketone A_4, all these solvents can be arranged in the sequence: MeOH > EtOH > Pr^nOH + 15% H_2O > Pr^iOH + 5% H_2O > Pr^iOH > Pr^nOH > Bu^iOH > Bu^nOH. The optimum activity and selectivity (94%) of the Ni–Co catalytic system with respect to C=C bonds of pseudoionone were achieved in isopropanol. This is explained by the fact that isopropanol shows the least tendency to be adsorbed on Group VIII metals and, therefore, it weakens the interaction between the ketone and $CoCl_2$ in the solution bulk to a lesser degree.

The kinetics of hydrogenation of β-ionone in the presence of Pd and Ni catalysts have been studied both in open and in closed systems with varying conditions of the reaction and the nature of solvent.[77-80]

Of interest are papers dealing with hydrogenation of polyunsaturated ketones having more complex structures.[81-87] A method for preparing higher saturated ketones in the presence of the Pd/Al_2O_3 catalyst with a palladium content of 0.05 to 5 mass.% is described in a patent.[82] The yield of 6,10,14-trimethylpentadecan-2-one (A_8, a C_{18} saturated ketone) reached 95%. For selective reduction of unsaturated ketones to saturated ketones, an effective industrial Pd-based catalyst (ShPAK-0.5, 0.5% Pd/Al_2O_3) has been chosen.[16,84-87] The components used for its preparation, Pd/Al_2O_3 and Al_2O_3, were studied by various physicochemical methods [IR spectroscopy, X-ray photoelectron spectroscopy (XPS), extended X-ray absorption fine structure spectra (EXAFS), electron microscopy, and adsorption, analytical, and X-ray methods]. In conformity with EXAFS data,[88] it has been noted that the Pd–Pd distance increases upon deposition of palladium by 0.007 nm, which is due to the need for palladium to fit into the structure of the carrier. The free energy of the deposited palladium [$E_{fr}(Pd_{3d_{5/2}}) = 335.6$ eV] is close to that of massive palladium. The layers situated near the surface of palladium reduced in isopropanol contain carbon (Pd/C ~ 73). During thermal desorption (TDS), peaks due to hydrogen with T_{max} = 331 and 448 °C were detected, associated with destruction of hydrocarbons on the catalyst surface. Statistical analysis of the results of an electron-microscopic study of the catalyst active layer has shown that surface particles measure 2–5 nm; capillary impregnation of a sample with isopropanol made it possible to determine the average diameter of pores (9.5 nm) and porosity (0.57).[16]

In the presence of the ShPAK-0.5 catalyst, the kinetics of hydrogenation of pseudoionone have been studied, P_{H_2}, T_c, c_0, and c_c being varied over wide limits.[16,84] When the Pd/Al_2O_3 catalyst is used for the reduction of pseudoionone, the n value in Eqn (4) is 1, as in the case of Pd/C. The experimental results on the hydrogenation of pseudoionone under various reaction conditions are adequately described by Eqn (2), which suggests that hydrogenation of pseudoionone on Pd/Al_2O_3 and Pd/C proceeds via a common mechanism.

Hydrogenation of 6,10,14-trimethylpentadeca-3,5-dien-2-one (A_6, a C_{18} unsaturated ketone) in the presence of Pd/Al_2O_3 also occurs according to a parallel-sequential scheme (Scheme 4).

In this case, the n value in Eqn (4) is 1 or 2.[16,86] Experimental data were fitted using Eqn (4), and the optimum model for the process of hydrogenation of ketone A_6, which takes into account adsorption of the components of the reaction system, has been suggested.

$$W_1 = \frac{a_1 x_1}{(x_1 + Q_2 x_2 + Q_3 x_3)^n} \frac{P_{H_2}}{1 + b_1 P_{H_2}}, \quad (6)$$

$$W_2 = \frac{a_2 x_1}{(x_1 + Q_2 x_2 + Q_3 x_3)^n} \frac{P_{H_2}}{1 + b_2 P_{H_2}}, \quad (7)$$

$$W_3 = \frac{a_3 x_2}{(x_1 + Q_2 x_2 + Q_3 x_3)^n} \frac{P_{H_2}}{1 + b_3 P_{H_2}}, \quad (8)$$

where $n = 1, 2$ and x_1, x_2, and x_3 are reduced concentrations of the unsaturated ketone A_6, 6,10,14-trimethylpentadeca-3-en-2-one (A_7), and the saturated ketone A_8, respectively. Parameters of Eqns (6)–(8) are listed in Table 1.

Table 1. The results of solving the inverse problem in terms of equations (6)–(8) for hydrogenation of ketone A_6 (50 °C).

$10^3 \times a_i$/mol² g⁻² s⁻¹ MPa⁻¹			b_i/MPa⁻¹			Q_2	Q_3
a_1	a_2	a_3	b_1	b_2	b_3		
3.51	1.43	0.77	0.93	1.00	1.35	2.11	0.62

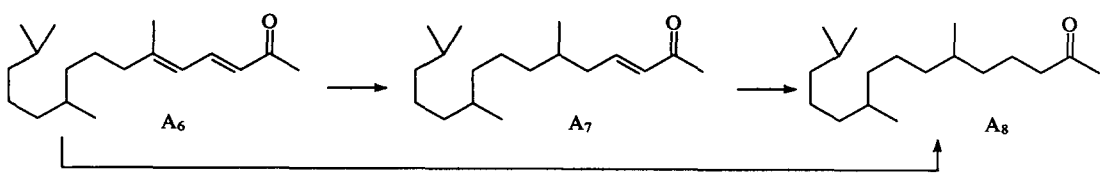
Comparison of the experimental and calculated curves (Fig. 2) showed that this model is in satisfactory agreement with the experimental observations: the error of the estimation of all the parameters of Eqns (6)–(8) lies within 10%. These equations attest to a complex mechanism of the hydrogenation reaction of ketone A_6.

In the physical justification of Eqns (6)–(8), we supposed[16] that the substrate is adsorbed on organometallic centres of the catalyst (Z')[89] that are formed as surface compounds, A_iZ' and $A_iZ'_2$, through the action of the substrate, solvent, and modifying additive. Hydrogen is activated on the metal atoms and diffuses to adsorbed substrate molecules.[90] Study of the influence of a competing inhibitor (pyridine) on the rate of hydrogenation of ketones A_1 and A_6, resorting to the XPS and TDS data, made it possible to conclude that the catalyst active centres have a complex structure; the IR spectra imply that the adsorption of ketones on the catalyst must be taken into account. The k_i, b_i, Q_i, and a_i parameters in Eqns (2) and (6)–(8) turned out to be complex combinations of constants.

It should be noted that in the presence of Pd/Al_2O_3, which is a selective catalyst of hydrogenation of polyunsaturated ketones, the saturated alcohol was formed neither under dynamic, nor under static conditions (the selectivity with respect to saturated ketones was 99.5%–99.7%).[91]

Metal-containing polymeric catalysts, for example those incorporating Rh, possess a number of advantages over traditional heterogeneous catalysts.[92,93] During the synthesis of a metallopolymer, formation of organometallic centres necessary for activation of the substrate is possible. To prepare rhodium-containing polymeric systems, the complex-formation reactions between rhodium chloride and rhodium carbonyl chloride and active olefin groups in a polymeric matrix have been

Scheme 4



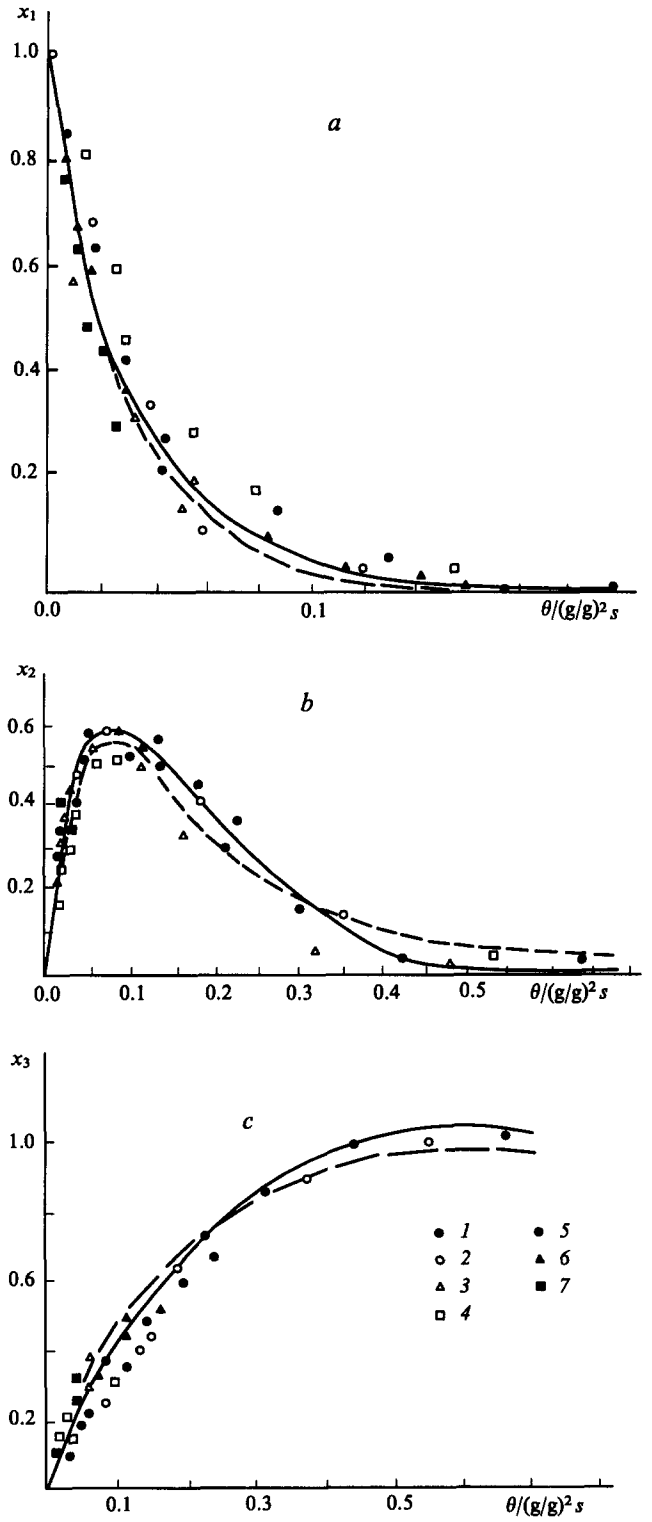


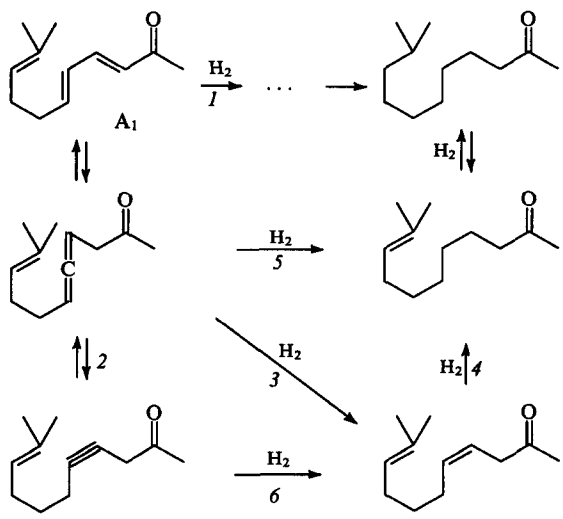
Figure 2. Generalised plots of the time variation of the composition of the reaction mixture during hydrogenation of ketones A_6 (*a*), A_7 (*b*), and A_8 (*c*) (Pd/Al_2O_3, $T = 25$ °C, $P_{H_2} = 2.5$ MPa). The continuous lines illustrate the results calculated according to model (6)–(8), the dashed lines correspond to the calculations according to the linear model, and the points are experimental results. q (g/g): (*1*) 37.5, (*2*) 71.4, (*3*) 75.0, (*4*) 107, (*5*) 143, (*6*) 250, (*7*) 750.

selected.[94] It was shown that the use of nonpolar solvents (benzene, toluene, hexane) results in deceleration of the hydrogenation. To the greatest degree this relates to hexane, possibly due to swelling of the polymeric catalysts in aromatic solvents, which results in increase in the number of available active centres. At the same time, polar aromatic compounds as well as THF, DMSO, and DMF are likely to be coordinated by the reactive centres of the catalyst, which leads to decrease in their activity. Good results were obtained when the hydrogenation of pseudoionone was carried out in alcohols. Isopropanol turned out to be the best, among the series of alcohols, as in the case of hydrogenation on the traditional heterogeneous catalyst, ShPAK-0.5 (Pd/Al_2O_3). Based on the study of the kinetics of hydrogenation of pseudoionone on a Rh-containing polymeric catalyst deposited on Al_2O_3 (Rh is twice deposited: on the polymer and on Al_2O_3), a kinetic model and a mechanism were proposed for the reaction. High stability of the Al_2O_3-deposited Rh-polymeric catalyst was noted.[95–97]

On an industrial scale, ketones A_1 and A_6 are produced by isomerisation of the corresponding allene ketones in ethanolic alkali. Hydrogenation of allene ketones in the presence of Ni and Pd catalysts was studied under static and dynamic conditions, the parameters of the process and the nature of solvent being varied over wide limits.[16] It was found that reduction of ketone A_1 occurs with a lower initial rate but much more selectively than that of ketone A_6. The selectivity of the hydrogenation of A_1 with respect to ketone A_4 in the presence of Raney Ni can be as high as 97.8%; that for the hydrogenation of A_6 with respect to A_8 is 53%.

The results of kinetic and spectroscopic studies suggest that in the presence of Pd/Al_2O_3 or the Ni–Co catalytic system, the reaction proceeds according to route (*1*) (Scheme 5) in all the solvents studied (C_1–C_4 alcohols of normal and iso structures, with or without addition of H_2O). In isopropanol in the presence of the Ni–Co catalytic system, route (*5*) is the predominant reaction path, and in the case of non-modified Raney Ni, routes (*2*) and (*6*) prevail.

Scheme 5



Analysis of the literature data on the selective hydrogenation of α, β-unsaturated and polyunsaturated ketones makes it possible to draw the following conclusions:

In the presence of platinum group catalysts, under mild conditions, the C = C bond in α, β-unsaturated ketones is reduced preferentially.

Pd- and Rh-containing polymeric and modified Ni catalysts (to a lesser degree) are the most selective catalysts of the hydrogenation of dienones and polyenones.

Highly selective addition of H_2 at the 1,2, 1,4, or 3,4 positions of the enone or dienone systems is possible, and C_{13} and C_{18} saturated ketones can be obtained from the corresponding allene ketones.

General features of the hydrogenation of unsaturated ketones have been identified:

Components of the reaction system affect significantly the selectivity and the activity of the catalyst with respect to double bonds of the ketone.

Interaction between the participants of the reaction, not only at the interface but also in the bulk of the solution, must be taken into account.

Heterogeneous catalysts can be modified not only by specially introduced additives but also by the solvent or substrate (this accounts for the observed nonlinear relations between kinetic parameters and the amount of catalyst).

Similar regularities are characteristic of the hydrogenation of acetylene alcohols.

III. Selective hydrogenation of acetylene alcohols

1. Catalysts for selective hydrogenation of C≡C bonds

A number of catalytic systems for selective hydrogenation of alkynes to alkenes have been described in the literature. Among these are homogeneous catalysts containing complexes of Group VIII metals (mostly Pd, Rh, Ni) with sulfur- and phosphorus-containing[98,99] ligands or nitrogen-containing organic chelating ligands (EDTA, ethylenamines, aminoacids, phenanthroline, morpholine, pyridine and its homologues, tertiary amines, etc).[100,101] Octylamine-based catalysts are most active in the hydrogenation of diphenylacetylene. Their selectivity with respect to the olefin amounts to 98%–100%. At the beginning of the reaction an induction period occurs, which disappears in the case where the complexes are first treated with hydrogen.[102]

However, homogeneous catalysts of the selective hydrogenation of acetylene compounds are not very effective from the technological standpoint. Therefore, in recent years studies on making them heterogeneous are being carried out.[103,104] In these studies, a modifying effect of oxygen and a substantial influence of a reduced hydrogen pressure ($\leqslant 0.01$ MPa) on the selective reduction of a C≡C bond to a C=C bond was found.[104] The selectivity with respect to olefin reaches 98%–99%. Unfortunately the above-mentioned papers contain no data on stability of the catalysts proposed.

Membrane catalysts based on Pd and its alloys have been considered as promising from the technological standpoint.[105–107] The high selectivity of conversion of acetylene alcohols in the presence of these catalysts is due to the fact that the concentration of hydrogen adsorbed on the catalyst surface and dissolved in its bulk can be controlled by varying the composition of the alloy and the hydrogen pressure at the operating side of the membrane. It was shown that these catalysts possess on average a 100-fold higher productivity per unit surface area than conventional catalysts,[108] the selectivity being 95%–99%.

However, supported catalysts are still the most technologically effective. One of the main lines of the search for selective catalysts of hydrogenation of acetylene compounds to ethylene compounds is modification of deposited Pd catalysts, which are most selective in the hydrogenation of a C≡C bond to a C=C bond. Heterogeneous catalytic systems for partial hydrogenation of a triple bond are listed in Table 2. Some authors (for example, Cerveny et al.[119]) attribute the enhanced activity and low selectivity of Pd/C with respect to formation of alkenes to the high degree of dispersion of the active metal on the carrier, however, they do not take into account the intensity of the interaction between the disperse phase and dispersion medium. On the contrary, Karturan et al.[128] have noted that Pd/SiO_2 possesses the maximum selectivity in the case where Pd is highly dispersed. Analysis of the data presented in Table 2 shows that the low-percentage Pd/Al_2O_3 catalyst modified with organic or inorganic substances is most widely used for the selective hydrogenation of C≡C bonds to C=C bonds.

Hydrogenation of dimethylethynylcarbinol. In a number of studies,[129–136] Pd catalysts modified with organic or inorganic additives were used for the selective hydrogenation of dimethylethynylcarbinol (DMEC, A_9, a C_5 acetylene alcohol) to the corresponding vinylic alcohol. For example, in a study of the reduction of carbinol A_9 yielding dimethylvinylcarbinol (DMVC, A_{10}, a C_5 ethylene alcohol) in the presence of 5%–20% $Pd/CaCO_3$ with addition of Zn, Cd, or Pb salts, it has been shown that the catalyst containing 20% Pd is the most selective. The dependence of the optimum modifier : catalyst ratio on the nature of the salt was noted; for Zn compounds this ratio is an order of magnitude higher, which is attributed to the lower adsorption ability of the Zn cation, as compared with Pb or Cd.[130]

It was found in a study of the hydrogenation of DMEC in the presence of 0.5% Pd/Al_2O_3 modified with the optimum amount of the specifically adsorbed Zn and Cd cations under static or dynamic conditions that the continuous process occurs with low selectivity, which, was suggested to be associated with transport phenomena.[129]

The selectivity of the reduction of DMEC to DMVC in the presence of the $Pd/CaCO_3$–$Zn(CH_3COO)_2$ catalytic system at a Zn : Pd atomic ratio of 0.75–5.87 was 92%–96% when 1 mole of H_2 had been absorbed; at this point the catalysate already contained 3.5%–5% of the saturated alcohol.[131] Introduction of nitrogen compounds (triethanolamine, triethylamine, NH_3) into this catalytic system suppresses hydrogenation of the C=C bond of the alcohol.

A catalyst for hydrogenation of DMEC to DMVC containing Pd and additives has been developed.[132] The laboratory and pilot

Table 2. Catalysts for the selective hydrogenation of C≡C bonds.

No. П/П	Catalyst, carrier, modifier, solvent, hydrogenation conditions	Ref.
1	Pd catalyst treated with alkali, 0–100 °C; 0.5–3.0 MPa	109
2	Pd/carrier (Al_2O_3, C, $CaCO_3$, $BaSO_4$, sepiolite), modified with heavy metal cations or organic amines	110, 111
3	the Lindlar catalyst, pyridine, in hexane	112
4	0.05% Pd/Al_2O_3	113, 114
5	0.05–5% Pd/Al_2O_3, $Pb(CH_3COO)_2$ or $Sn(CH_3COO)_2$ (modifier : catalyst = 2 : 5)	115
6	Pd/Al_2O_3 – Zn and/or, Cd, Bi and/or Tl	116
7	Pd/Al_2O_3 – Group VIB metals	117
8	Pd/Al_2O_3,$Pd/CaCO_3$, Pd/C	118
9	Pd/C, Pd/SiO_2 – Pb, Tl	119
10	0.1–60% of the hydrogenating Group VIII metal deposited on a carrier with 0.001%–10% of (Cd, Cu) oxides and 0.5–2% of K_2O added (relative to the overall weight of the catalyst)	120
11	Pd/carrier, Group IV elements (Sn or Pb)	121–123
12	Pd–Ag (Pd : Ag = 10 : 1)	124
13	Pd, modified with Ge, Sn, Pb or Sb	125
14	Pd/Al_2O_3 (0.3% Pd) with a Pd particle size of 8 nm	126
15	Zn – Cu, modified with alkali metals	127

tests on the hydrogenation of DMEC to DMVC showed that the Pd–Zn catalytic system is more active and selective than Pd–Pb.[133] The activity in the reduction of DMEC of low-percentage SiO_2-deposited Pd catalyst modified with chlorine-containing complexes of Ru(IV), Ir(IV), Rh(III) has also been studied.[134] In view of the fact that there is no additivity in the effect of the components of a catalyst on its activity and selectivity, it was suggested that heteronuclear metal complexes formed on the surface of the carrier are responsible for a definite reaction pathway. As has already been noted, the selectivity of the hydrogenation of DMEC to DMVC can be increased by using mixed catalysts. For this purpose, Pd–Cu/TiO_2 catalysts with various proportions of the active phase have been suggested.[135] The apparent activation energy for the hydrogenation of DMEC[136,137] varies from 16 to 50 kJ mol^{-1} and is determined by the nature of the components of catalytic system.

Hydrogenation of 3,7-dimethyloct-6-en-1-yn-3-ol. There are considerably fewer papers dealing with hydrogenation of 3,7-dimethyloct-6-en-1-yn-3-ol (DOL, A_{11}, a C_{10} acetylene alcohol). Interesting results have been obtained with Pd-based catalysts, which possess the highest selectivity.[138] When C_2–C_4 alcohols with the normal or branched structure are used as solvents, the proportion of linalool (LH, A_{12}, a C_{10} ethylene alcohol) in the catalysate is lower in the latter case. The selectivity of hydrogenation of DMEC to DMVC is higher than that of DOL to LH in all the alcohols. The apparent activation energy for the hydrogenation of DOL in the presence of Pd black amounts to 8.4–12.6 kJ mol^{-1}, i.e. it is lower than that for DMEC. At the same time, it has been shown[139] that lengthening of the hydrocarbon skeleton of acetylene alcohols from 5 to 8 atoms should be favourable for increase in the yield of the corresponding ethylene derivative in the hydrogenation process. Problems of selectivity of the catalytic hydrogenation of DOL have been considered in the literature.[118,140] Pd/$CaCO_3$ modified with Pb was used as the catalyst. However, the highest selectivity with respect to the conversion of DOL into LH is exhibited by γ-Al_2O_3-deposited Pd catalysts with a Pd content of 0.5%.[138] When the content of the active component is increased to 2%, the selectivity diminishes slightly, and when it is increased to 5%, the selectivity decreases substantially. Analysis of the degree of dispersion of Pd particles and their size distribution in the catalysts with different contents of the active component has shown that increase in the content of the active component results in increase in the proportion of particles of size 3.5–5 nm. The content of the dissolved hydrogen, promoting the saturation of a double bond,[128] in metal particles of diameter 5 nm corresponds to the ratio H : Pd = 1.[141,142] This is apparently the reason for the higher selectivity of 0.5% Pd/γ-Al_2O_3.

The influence of the hydrogen pressure in the range 1.01 to 5.05 MPa on the hydrogenation of DOL in the presence of Pd/Al_2O_3 has been studied.[138,143] A decrease in the selectivity at pressures above 3.03 MPa was observed. In the cases where the Pd/Al_2O_3 and Pd/$BaSO_4$ catalysts were used, the apparent activation energies were found to be approximately equal, while the reaction order with respect to the substrate is close to zero (in all the solvents) in the former case and is equal to unity (in EtOH) in the latter case. In addition, slight adsorption of the reaction products was observed.

The selectivity of hydrogenation of DOL, like that of DMEC, increases, when modifying additives are introduced into the reaction mixture.[144–146] A kinetic model for this reaction has been proposed.[147,148] Pd/C proved to be the least selective of the catalysts studied.[140,146]

Of interest are data on the hydrogenation of C≡C bonds of acetylene alcohols to C=C bonds in the presence of Pd immobilised in a polymeric matrix.[149]

This catalyst deposited on Al_2O_3[150] was used for preparing linalool. This system, like Rh-polymer/Al_2O_3 used for hydrogenation of unsaturated ketones,[95] possesses a series of advantages over the traditional heterogeneous catalysts, namely, high stability and mechanical strength, and requires no modifying additives (chemical poisons).

Hydrogenation of 3,7,11-trimethyldodec-1-yn-3-ol and 3,7,11,15-tetramethylhexadec-1-yn-3-ol. For hydrogenation of 3,7,11,15-tetramethylhexadec-1-yn-3-ol (dehydroisophytol, DHIP A_{13}, a C_{20} acetylene alcohol), the Lindlar catalyst prepared from commercial $Pb(CH_3COO)_2$ has been shown[151] to be more selective than this catalyst prepared from a preliminarily purified specimen. This fact led Rajaram and coworkers to the conclusion that microimpurities present in the commercial $Pb(CH_3COO)_2$ facilitate the selectivity of the process. In the list of these microimpurities they included Cu^{2+}, Cd^{2+}, Mn^{2+}, Fe^{3+}, and Co^{2+} ions and studied their effect on the selectivity of the Lindlar catalyst in the hydrogenation. The best results were obtained in the presence of $MnCl_2$, where the selectivity amounted to 97.2%.

A method has been patented for the selective reduction of acetylene alcohols in the presence of a Pd–M/carrier system (M is Zn, Bi, Cu, etc., the carrier is $CaCO_3$, $BaSO_4$, etc.) and a sulfur-containing or amino compound that are simply mixed with the Pd catalyst. The yield of isophytol was 98.3% and that of linalool was 98.6%.[152] Some authors recommend organophosphorus compounds as modifying additives for Pd catalysts of the hydrogenation of C_{20} acetylene alcohols and 3,7,11-trimethyldodec-1-yn-3-ol (dehydronerolidol, DHNL, A_{14}, a C_{15} acetylene alcohol).[153]

The hydrogenation reactions of C_5, C_{15}, and C_{20} acetylene alcohols to the corresponding ethylene analogues on Pd catalysts deposited on carriers of acidic or alkaline nature in the presence of iodides have been studied[154] under static and dynamic conditions in various solvents, varying the temperature, the hydrogen partial pressure, and the initial concentration of acetylene alcohol. An increase in the temperature and pressure was found to diminish the selectivity of the process. In the static system, the highest selectivity with respect to vinylcarbinol was achieved with Pd/$CaCO_3$ and Pd/ZnO–KI homogeneous-heterogeneous systems in MeOH. The author believe that the high selectivity observed with these carriers is due to their basic properties. They suggest that the reaction has the zeroth order with respect to substrate, though the relationships presented indicate that the reaction rate diminishes with decrease in the concentration of the substrate in the solution. The Pd/ZnO–KI system in EtOH was recommended for the reaction carried out under continuous conditions. However, the high starting selectivity of this catalyst (97.5%) quickly drops, due to gradual washing out of KI, which is readily soluble in EtOH.

A method of preparing ethylene alcohols from acetylene alcohols in the presence of the ShPAK-0.5 (0.5% Pd/Al_2O_3) catalyst modified with $Zn(CH_3COO)_2$, pyridine, and alkali has been developed.[16] The highest selectivity with respect to C_5, C_{10}, C_{15}, and C_{20} (99.2%–99.8%) ethylene alcohols in MeOH is achieved at a reduced hydrogen pressure. When catalysts with a controlled distribution of the active component[155] over a carrier grain have been used, high selectivity with respect to isophytol (98%) was achieved in the dynamic regime.[16] This is probably due to the absence of the internal-diffusion retardation.

Despite the fact that the use of modified Pd/Al_2O_3 for selective hydrogenation of the C_{15} and C_{20} acetylene alcohols is promising, studies aimed at the development of cheaper, more stable, more active, and no less selective catalysts are being carried out.[16] The research has several aims. The first of them is the development of novel Pd catalysts on polymeric carriers, the second is elaboration of methods for selective hydrogenation of acetylene alcohols in the presence of palladium-free catalysts, such as metal phthalocyanines (PcM) on oxides. PcM were chosen as the active component of the catalyst, in order to simulate the 'organometallic' active centre.

The selective hydrogenation of the A_{13} alcohol in the presence of Pd-containing polymeric catalysts with reaction parameters varying over wide ranges revealed the optimum substrate : catalyst

ratio, in terms of selectivity and duration of the reaction. This ratio confirmed that the formation of reactive complexes responsible for the reduction of the triple bond of the alcohol to the double bond is affected by the medium. Introduction of pyridine into the reaction system increases the selectivity of the conversion of the acetylene alcohol to the ethylene alcohol to 98%–99.3%.[149]

The selective hydrogenation of acetylene alcohols in the presence of PcM (M = Pd, Ni, Cu, Co) deposited on oxides (Al_2O_3, SiO_2) has been studied. The conditions in which the reaction was carried out, the nature of solvent, the method of the PcM deposition, and the content of the active component on the carrier have been varied. The experiments were carried out in the static and dynamic regimes.[16,156]

It was found[16] that transition from a polymolecular layer of PcM on the oxide carrier to a monomolecular layer results in an increase in the effectiveness of the catalytic action of immobilised PcM. The method of the PcM deposition on the oxide (from concentrated H_2SO_4 or from benzene) determines not only the activity of the catalyst but also the mechanism of its action. To elucidate the mechanism of the hydrogenation catalysis by PcM, kinetics of the hydrogenation of A_9 and A_{14} alcohols in the presence of $PcCo/SiO_2$ (0.2% Co, PcCo was deposited on the oxide from a solution in H_2SO_4) and $PcNi/Al_2O_3$ (0.2% Ni, PcNi was deposited on the oxide from a benzene solution) were studied. Under optimum conditions, the yield of the target product amounted to 99.2%–99.8%.

Analysis of the published papers allows the following conclusions to be drawn:

the most selective heterogeneous catalysts for hydrogenation of a triple bond to a double bond are Pd catalysts deposited on nonporous carriers ($BaSO_4$, $CaCO_3$) or on porous carriers (Al_2O_3, SiO_2) with small particles of the disperse phase (the latter has been satisfactorily confirmed by studies, which showed the dependence of the selectivity on the depth of the carrier porosity[128]);

modification of heterogeneous catalysts by inorganic additives of basic character, phosphorus- and sulfur-containing compounds, or salts of various metals favours an increase in the selectivity; the Pd–Zn system exhibits a fairly high activity with no loss in the selectivity;

catalytic systems based on PcM and Pd-containing polymers (on inorganic carriers) used for partial hydrogenation of C_5, C_{10}, C_{15}, and C_{20} acetylene alcohols possess high selectivities;

Pd/C has a low selectivity, which is attributed to the high degree of dispersion of this catalyst. The strength of the interaction between the disperse phase and the dispersion medium and thus the selectivity of the process can be controlled by varying the nature of the solvent and the concentration of the substrate.

2. The mechanism of the modification of catalysts for the selective hydrogenation of C≡C bonds

In a study of the selective hydrogenation of unsaturated ketones, interaction of the introduced additives with the solvent and the substrate within the bulk of the solution and an influence of the modifier on the heterogeneous catalyst have been observed.[16] The role of the modifier of catalysts of partial hydrogenation of C≡C bonds is that they poison the active centres at which further hydrogenation of the ethylene bond or hydrogenolysis of the substrate would have occurred[151,157,158] and promote the centres responsible for the saturation of the triple bond.[138] For example, it has been shown for Pd-containing catalytic systems that Pb, which blocks a part of the Pd surface, decreases the total adsorption of the hydrocarbon.[157] The centres with high bond energies are blocked first and, therefore, a sort of levelling of the substrate–metal bond energies occurs. The action of the modifying additives is explained as follows: the energies of metal–hydrogen and metal–substrate bonds and also the amount of hydrogen adsorbed change; the rate of release of the dissolved hydrogen decreases, since as a result of modification the activation energy of hydrogen desorption increases from 84 to 146.7 kJ mol^{-1}.[138,159] Thus, the addition of a modifying metal (for example, Pb or Zn) to the major component of the catalyst (for example, Pd) may change the electronic properties of the latter (the ligand effect) or the geometry of its surface.[160] The latter phenomenon is caused by a cluster effect or an ensemble effect.[161]

The cluster and ligand effects in bimetallic catalysts have been considered in detail in a review.[161] Clear-cut is the effect of modifying additives on the size of clusters of the active metal, which, in turn, determines the adsorption ability, activity, and selectivity of a catalytic system. The ligand effect, which is manifested as an electronic interaction between the modifier and the major component of the catalyst, causes the formation of strong bonds in the reactive complex. Charge transfer from the metal to the modifier or conversely is determined by the difference between the electronegativities of the components. In addition, the second component prevents carbonisation, poisoning, and agglomeration of a multicomponent catalyst. It also acts as a diluent of the surface, so that, of all the thermodynamically possible routes to the substrate transformation, only that reaction selectively occurs which requires a small ensemble. A definite concentration of the specifically adsorbed ions results, so that the dissolved hydrogen becomes the main hydrogenating agent.[159] However, this is inconsistent with the inferences of some researchers, who showed experimentally that the dissolved hydrogen exerts a negative effect on the selectivity of hydrogenation of acetylene compounds.[128]

Study of the thermal desorption of hydrogen and carbon monoxide from $Pd–Pb/Al_2O_3$ catalysts led Karski and Paryjczak[162] to the conclusion that the introduction of Pb into Pd/Al_2O_3 results only in a decrease in the amount of the gases sorbed, but causes no noticeable change in the activation energy of desorption.[162] In other words, these authors observed only the manifestation of the cluster effect.

Investigation of the mechanism of the action of poisons that enter in the composition of the Lindlar and Rosenmund catalysts is of some interest.[163] Analysis of the extensive literature data on the Lindlar catalyst and various methods for its modification, allowed the authors to conclude that the poisons are not involved in the catalytic process and do not occupy the active centres; they only change the structure of the catalyst surface. An electron-microscopic study showed that under the action of amines, species with low surface areas are formed.

Regarding the action of the Lindlar catalyst and the Lindlar catalyst–$MnCl_2$ catalytic system, two suggestions have been made:[151] 1) active ensembles for hydrogenation of a triple bond to a double bond and for hydrogenation of a double bond to a single bond are dissimilar; 2) there occurs a 'mobile' distribution of the cations of the modifying metal over the Pd surface. These suggestions have been confirmed by experimental results.

Effects of various substances, either present in the reaction mixture or added to it, on the selectivity of the catalytic hydrogenation of unsaturated compounds have been considered. It was noted that the mechanism of the action of additives is usually complex, nevertheless, in a number of cases it can be explained in terms of the ligand effect.[164] Introduction of electron-donor compounds, for example, piperidine, in a catalytic system results in an increase in its activity and selectivity with respect to the conversion of acetylenes to olefins.[165]

Comparing electronegativities,[166] electronic work functions, the first and second ionisation potentials, and standard electrode potentials[167] relative to Pd of the modifiers recommended in the literature, one may infer that the magnitudes of these parameters characterise to a certain extent the interaction between Pd and a modifier provided that there is information on the modification mechanism. For example, reasoning from electonegativities and assuming, as was done by Lindlar,[144] that a Pd–modifier catalytic system incorporates the modifier in the form of metal, one may conclude that modifiers act with respect to Pd as donor ligands.

A number of researchers, who have studied the action of a solution of $ZnCl_2$ (or $CdCl_2$) in a hydrogen atmosphere on the

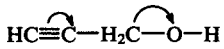
reduced 1% Pd/Al_2O_3 catalyst, inferred that complex surface clusters, $Pd-Zn/Al_2O_3$ and $Pd-Cd/Al_2O_3$, are formed.[168]

Of the possible modifiers for 0.5% Pd/Al_2O_3, $Zn(CH_3COO)_2$ was chosen.[16,169-171] The modified catalyst proved to be more selective in the hydrogenation of the A_{14} carbinol to isophytol (IP, A_{15}, a C_{20} ethylene alcohol) (93.2%) than the nonmodified catalyst (76%). Zn probably acts as a donor of electrons with respect to Pd and, therefore, it increases the possibility of the charge transfer to the acetylene alcohol. In addition, the metal–modifier bifunctional active centre levels the negative effect of the dissolved hydrogen. Finally, Zn prevents coke formation. All these effects ensure the higher selectivity of the modified catalyst. Modified Pd/Al_2O_3 was studied by various physicochemical methods. It was found that due to the modification of the catalyst, its porosity decreases from 0.57 to 0.04 and the effective pore radius decreases from 9.5 to 0.7 nm; this diminishes the influence of the internal diffusion in the hydrogenation of A_{14} in the kinetic regime. The increase in the degree of dispersion of surface Pd particles (2–3 nm) lowers the amount of the dissolved hydrogen and results in a higher selectivity of the conversion of the A_{14} alcohol to A_{15}. The decrease in $E_b(Pd_{3d_{5/2}})$ by 0.6 eV is attributed to the electron-donor properties of Zn. Based on the EXAFS spectra, the Pd–Zn distance was determined, and it was concluded that the interaction between Pd and Zn occurs via a ligand. Further modification of the catalyst with organic (pyridine) or inorganic (KOH) bases (base : catalyst = 1 : 10) made it possible to achieve the highest selectivity of the hydrogenation of the A_{14} acetylene alcohol to the A_{15} ethylene alcohol in the presence of this catalyst (99.2%).

3. Mechanism of the adsorption and catalysis of acetylene compounds

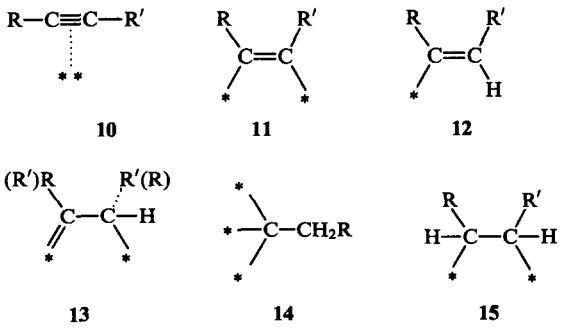
Acetylenic compounds, like ethylene compounds, can be adsorbed by both associative and dissociative mechanisms.[31,172] In the presence of hydrogen, acetylenes are adsorbed on the catalyst surface mostly by an associative mechanism.[173]

Considering adsorption of acetylene alcohols with various carbon chain lengths, one should take into account both inductive and mesomeric effects,[174] the latter withdrawing electron density from the triple bond to the oxygen atom.



With increase in the carbon chain length, the inductive effect grows, which acts in the opposite direction, i.e. tends to increase the electron density at the C≡C bond. These effects, together with steric factors, govern the adsorption and catalysis in the case of acetylene alcohols.

It has been suggested that selective catalytic hydrogenation of acetylene alcohols involves formation of the following surface structures:[151]



10 **11** **12**

13 **14** **15**

* is an active centre of the surface;

** is a diatomic active centre of the surface.

Intermediate compounds **10–12** may arise upon the reduction of an acetylene to an olefin, while structures **13–15** are intermediates on the way to the fully reduced products.

According to quantum-chemical calculations, the most probable mechanism of the hydrogenation of DMEC to DMVC involves formation of negatively charged forms of DMEC on the metal surface, though this does not rule out the possibility that the reaction occurs via an electronically excited form of DMEC, i.e. the participants of the catalytic system (modifiers, solvent) should be chosen in such a way as to provide the predominant electron transfer from the metal to the substrate.[175] Karavanov et al.[176] believe that the rate-determining factor in the hydrogenation of linalool is addition of the first mole of hydrogen.

All the foregoing attests to complexity of mechanisms of the catalysis and adsorption of acetylene compounds. This is probably due to the fact that active centres with different coordination numbers exist on the catalyst surfaces. The active centres with high coordination numbers, where a competing mechanism of adsorption is possible, are likely to prevail at faces of crystals. On the contrary, active centres with low coordination numbers, that favour formation of an involved multi-ligand complex on chemisorption, predominate at corners, edges, and defects. It should be noted that those alkynes[151] are involved in the complex formation, which change the surface structure of the catalyst in the course of the adsorption and catalysis.

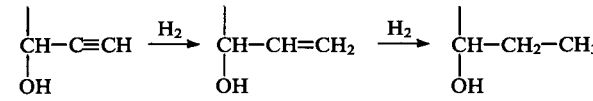
In order to identify details of the mechanism of the selective hydrogenation of acetylene alcohols, kinetics of hydrogenation of C_5, C_{15}, and C_{20} alcohols under static conditions have been studied, such parameters as T_c, P_{H_2}, c_O, c_C, and the nature of solvent being varied.[16]

Using Eqn (4) and taking into account the formal expression

$$W_1' = \frac{a_i x_i}{xX_1 + Qx_2} \frac{P_{H_2}}{1 + b_1 P_{H_2}}, \qquad (9)$$

where x_i are the reduced concentrations of acetylene ($i = 1$), ethylene ($i = 2$), and saturated alcohols ($i = 3$), for the reaction sequence depicted in Scheme 6, we managed to fit the experimental data on the hydrogenation of acetylene alcohols in methanol (Fig. 3).

Scheme 6



Based IR spectroscopic data, acetylene and ethylene alcohols were arranged, in terms of their adsorption ability, in the sequence $C_{20} > C_{15} > C_5$; the selectivity of their hydrogenation changes in the reverse order.

It should be noted that the generalised curves (Fig. 3) have an induction period at $0 \leqslant \theta \leqslant \theta_i$, the duration of which depends on the nature of alcohol. The above-given equation (9) does not hold in this region. The experimental data in this region are adequately described by the following relation:

$$\frac{dx_1}{d\theta} = -\frac{B}{x_1^n}, \qquad (11)$$

where B is a parameter.

The results of the interpretation of the experimental data on C_5, C_{15}, and C_{20} alcohols are presented in Table 3. The induction period has been attributed to the formation of a hetero-ligand reactive complex, which is responsible for the selectivity of the process, on the catalyst surface. The higher the molecular mass (M) of the alcohol, the stronger is its coordination with the catalyst, the lower is θ_i and the selectivity of the process.

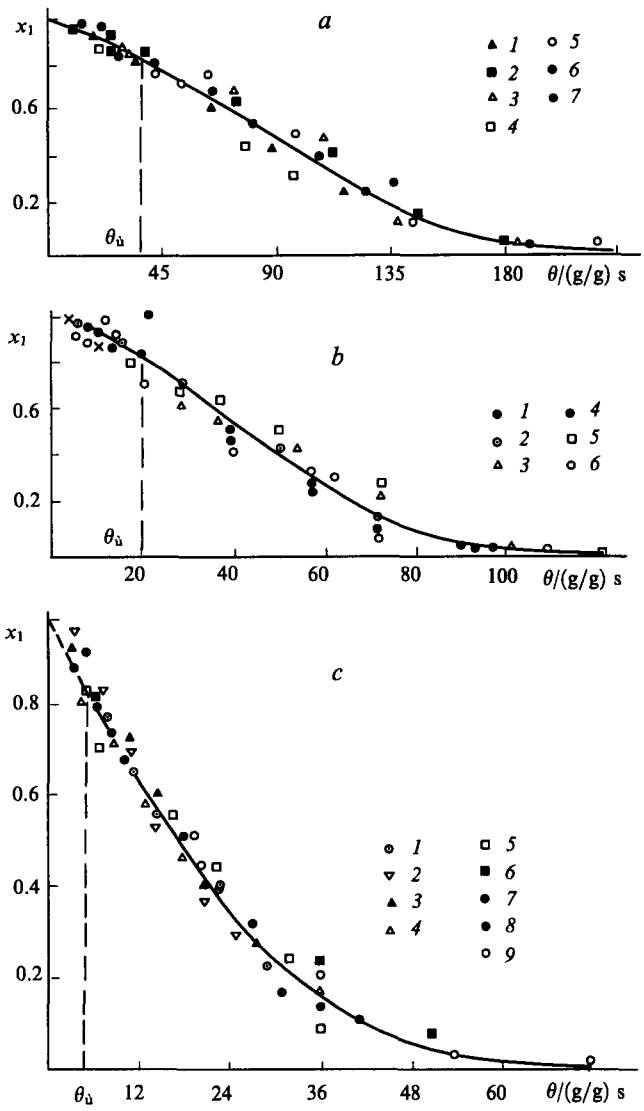


Figure 3. The dependence of x_1 on θ during hydrogenation of acetylenic alcohols A_9 (*a*), A_{13} (*b*), and A_{14} (*c*).
(*a*) T = 60 °C, P_{H_2} = 0.04 MPa, q(g/g): (*1*) 33, (*2*) 50, (*3*) 25, (*4*) 25, (*5*) 14, (*6*) 13, (*7*) 63;
(*b*) T = 40 °C, P_{H_2} = 0.07 MPa, q(g/g): (*1*) 55, (*2*) 50, (*3*) 30, (*4*) 15, (*5*) 15, (*6*) 100;
(*c*) T = 40 °C, P_{H_2} = 0.07 MPa, q(g/g): (*1*) 250, (*2*) 250, (*3*) 250, (*4*) 200, (*5*) 175, (*6*) 125, (*7*) 100, (*8*) 88.5, (*9*) 50.0

Table 3. The effect of the nature of alcohol on the characteristics of the induction period and the selectivity (S) of the process (T = 40 °C, P_{H_2} = 0.07 MPa).

Acetylenic alcohol	$n+1$	θ_i	S(%)
C_5	1.50	82.8	98.6
C_{15}	1.22	20.0	97.6
C_{20}	1.16	5.0	85.3

Analysis of the induction periods for acetylene alcohols affords the following relationship:

$$\theta_i = \frac{126\,764}{M^{1.65}} \quad (M^{n+1} = \text{const}). \qquad (12)$$

On the basis of this equation, the θ_i and n values for dehydrolinalool were calculated: θ_i = 28 (g/g) s and $(n+1)$ = 1.32, which agrees with experimental results.[16]

Owing to the competing character of adsorption from solutions, the adsorption of substrates may be considerably affected by the ability of the solvent to solvate reactants and to be coordinated by the catalyst. When considering multi-component multiphase systems, one should take into account the strength of the interaction between the disperse phase and the dispersion medium and the phenomenon of drainage[177] of the dispersion medium from the gap (pore) formed by the lyophilic disperse phase. This accounts for the fact that the hydrogenation of A_{13} in isopropanol involves higher energetic barriers (45 kJ mol^{-1}) than that in methanol (25 kJ mol^{-1}) and that of all the solvents studied, methanol provides the optimum selectivity with respect to ethylene alcohols.

As a result of studies on adsorption and using IR spectroscopic data, we revised[16] the sites of the coordination of H_2 and acetylene alcohol to a PcM molecule. It turned out that the alcohol is coordinated by the nitrogen atoms of the azo bridges. At low P_{H_2} values, hydrogen is predominantly coordinated to the central metal atom, while at elevated P_{H_2} [10.1 MPa] it is coordinated to both the metal atom and the organic ligand.

Analysis of the literature data on the selective hydrogenation of acetylene alcohols in the presence of PcM attached to inorganic carriers, Pd-containing polymeric catalysts, and modified Pd catalysts made it possible to identify some general regularities: the reaction proceeds via a hetero-ligand reactive complex (solvent, substrate, hydrogen, catalyst, modifier, and carrier), which has a multilayer structure; all the participants of the complex (their nature and amount) exert a mutual influence on the catalytic activity and selectivity of the process; the reactants are activated on different active sites ('metallic' or 'organometallic'). The same regularities were found for the hydrogenation of unsaturated ketones. The catalytic system should be regarded as a homogeneous-heterogeneous system. The validity of this description is confirmed by the observed non-linear dependences of the reaction rates on the ratio between the concentrations of the participants of the reaction.

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