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Bimetallic nanoalloys in heterogeneous catalysis of industrially important reactions: synergistic effects and structural organization of active components

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The review is concerned with correlations between the synergistic effects and structural organization of the surface of bimetallic alloys that are used as active components of catalysts for selective hydrogenation of organic compounds and for CO oxidation in hydrogen-rich mixtures. Studies on the preparation of novel highly efficient catalysts using modern theoretical approaches, computer-assisted molecular design and original synthetic procedures are considered. It is shown that introduction of the second metal into the monometallic catalyst and subsequent formation of alloy particles with modified structure of the surface and near-surface layers leads to nonadditive enhancement of catalytic activity and/or selectivity.
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I. Introduction

Heterogeneous catalysis is a branch of chemistry that is immediately related to technologies of preparation and stabilization of nano- and ultradispersed metal particles.[1,2] At present, active, selective and stable catalysts based on supported metal particles play an important role in chemical and petrochemical industries. They are used to carry out large-scale processes, such as hydrogenation, cracking, polymerization, hydrotreating and oxidation.[1] The performance of supported metal particles is intensively tested in relation to new catalytic reactions of production of fuel components using renewable raw materials and alternative for the development of compact fuel cells.[3–8] Considerable attention from manufacturers of mobile devices (notebooks, cell phones, smartphones, pocket PC) to fuel cells gives an impetus to research on the generation of hydrogen gas from methanol, hydrogen cleaning from carbon monoxide[3–8] and acceleration of electrochemical reactions.[9,10] In this connection, researchers face some new challenges, *e.g.*, achievement of high catalytic activity at reduced temperatures (this is atypical of heterogeneous catalysis) and

attainment of high sorption capacity of the catalyst with respect to hydrogen within the limits specified by particular $I-V$ curves. To solve these and other nontrivial catalytic problems, systems based on immobilized bi- and polymetallic alloy nanoparticles are used with increasing frequency.[11–15]

The history of the term 'alloy' in catalysis is tricky[16,17] and can be explained as follows. The chemical composition of the surface of a Pt–Re catalyst of reforming varies in the course of reaction, *viz.*, metals are transformed to sulfides. *In situ* studies showed that the role of catalysts is played by sulfides rather than the alloy particles. This is a good illustration to a problem faced by the research community in the late 1980s. It can be formulated as follows: what is the correct name for such 'dynamic' catalysts?

This problem was considered in detail in a review by Ponec,[17] who concluded that catalysts based on 'alloys' mean systems containing bi- or polymetallic compositions as active phase. In this review, we will follow this definition.

All bi- and polymetallic alloys can be divided[17] into

— solid solutions (single-phase alloys),

— individual compounds of constant composition (so-called intermetallies),

— systems composed of individual components (bi- and multiphase alloys), and

— so-called surface alloys that can be formed by metals of limited solubility.

Based on this classification, the title of this review includes the term 'bimetallic alloys' in order to emphasize that we focus on just this class of alloys. However, taking into account the possibility of significant structural changes in the active components of bimetallic alloys in the course of the reaction, other classes of polymetallic systems may also be involved in conceptual consideration.

Often, the properties of bi- or polymetallic catalysts can be described by the sum of the properties of monometallic analogues. For instance, the activity of a Pt–Ni catalyst for the hydrogenation of benzene[18] is approximately equal to the sum of the activities of the Pt and Ni catalysts. The selectivity of skeletal isomerization of n-decane[19] on a Pd–Fe catalyst is comparable with that of the process conducted on a mechanical mixture of the Pd and Fe catalysts. In some cases, the activity (selectivity or stability) of a bi- or polymetallic catalyst exceeds the sum of activities (selectivities or stabilities) of the monometallic constituents. This phenomenon is called synergistic effect; correspondingly, catalysts responsible for this effect are called synergistic catalysts. Examples of a synergistic effect in catalysis will be considered below.

The rate constants for hydrogenation of unsaturated aldehydes on Co–Pt, Co and Pt catalysts are 4×10^{-3}, 0 and 3×10^{-5} mol litre^{-1} min^{-1}, respectively.[20] The rates of the hydrogenation of acetylene[21] and steam reforming of glycerol into syngas[22] using Au–Ni catalysts are 20 to 100 times higher than those achieved with catalysts based on Au or Ni. The conversion of methane to syngas on the Ni catalyst decreases from 100% to 53% after 70 h. The introduction of zirconium additives into the nickel phase abruptly stabilizes the situation, namely, the conversion on the Ni–Zr system is 91% after 100 h of continuous operation.[23]

The nature of the synergistic effect in catalysis has been intensively debated in original studies (see, *e.g.*, Refs 20–35). A number of them are devoted to the types of physicochemical interactions between components of polymetallic systems that lead to synergistic effect in catalysis.[24,28–35] A unique attempt to a systematize the mechanisms of catalytic action of synergistic catalysts was made by Shi.[30] The value of two recent reviews[31,32] concerning catalysis on synergistic catalysts consists in that their authors attempted to classify synergistic catalysts with respect to their compositions and structures[31] and to the types of reactions being catalyzed.[32] An undoubtful advantage of these reviews is the breadth of coverage of the literature on synergistic catalysts and a large number of summary sheets that include the compositions and activities of catalysts in various reactions.

This review is concerned with synergistic catalysts containing bimetallic nanoalloys as active components. We briefly outline methods for the synthesis and stabilization of particles of bimetallic alloys, present information on the structure of supported alloy particles and describe modern methods of investigation of the morphology and electronic structure of such particles. We will discuss the most remarkable, in our opinion, studies on enhancement of the activity/selectivity of catalysts based on alloy nanoparticles in the industrially important reactions of selective hydrogenation of organic substrates and CO oxidation in hydrogen-rich mixtures.† The main goal of this review is to analyze the mechanisms of structural and electronic organization of the surface of nanoalloys and, correspondingly, adsorption sites upon the introduction of the second metal, which lead to a synergistic effect, *i.e.*, an abrupt increase in the activity, selectivity or stability of the catalysts based on nanoalloy particles. The emphasis is placed on the studies on preparation of novel high-performance catalysts using modern theoretical approaches, computer-assisted molecular design and original synthetic procedures.

II. The synthesis and structure of catalysts based on metallic nanoalloys

1. Methods for synthesis of bimetallic nanoalloys for catalysis

Numerous studies reporting manifestation of the synergistic effect when using polymetallic catalysts are available. On the one hand, they are devoted to the development of synthetic approaches to targeted modification of the structure of nanosized active components on the molecular level. On the other hand, they are aimed at studying diverse catalytic reactions in which the structure and electronic organization of active components influence the catalytic properties. Bimetallic nanoalloys can be synthesized by different methods (in, *e.g.*, solution, gas phase or by coating precursors onto solid substrates), some of them being analogous to fundamental methods for the synthesis of monometallic nanoparticles.‡

Wei *et al.*[40] presented a summary sheet for methods and efficient synthetic routes to bimetallic nanoalloys. They characterized main features of each approach, considered their advantages and drawbacks and gave examples of bimetallic catalysts prepared by these methods. Following

† This reaction is also called PROX (an acronym for PReferential OXidation).

‡ For detailed consideration of these problems, the reader is addressed to, *e.g.*, Refs 14 and 36–39.

a classification used by Hutchings and co-workers,[41] the main methods include:

— chemical reduction,
— thermal decomposition of precursors,
— electrochemical syntheses,
— radiolysis and
— sonochemical synthesis.

In turn, chemical reduction is divided into co-reduction, reduction of bimetallic complexes and successive reduction. Template synthesis involving the introduction of a structure-forming component during the formation of the metal-containing system is also used to obtain bimetallic materials with specified nanostructure. The technique is based on the same principles as the successive reduction method, but the versatility of the examples produced by template synthesis allows it to be treated as a separate subcategory.

It should be noted that, in spite of a variety of methods for preparing bimetallic nanoparticles, they are of limited use for the synthesis of catalysts. Methods for the synthesis of nanomaterials should be modified to meet the following requirements:

— metal (active) sites in catalysts should be accessible to reactants;

— the stabilizing ligands used in the synthesis of bimetallic materials to preclude aggregation should not poison the active sites;

— bimetallic nanomaterials should be sufficiently stable under the catalytic reaction conditions.

During decades, the army of researchers working on the search for and preparation of novel efficient heterogeneous catalysts have used methods of traditional 'wet' sol–gel chemistry.[13,42–45] The essence of these processes is to prepare solids from homogeneous or colloid (sol) solutions using various techniques including rapid precipitation, co-precipitation, slow homogeneous precipitation under controlled hydrolysis, sol–gel transitions, self-assembly on the molecular level, crystallization, *etc*. These processes can proceed under different conditions, *e.g*., in quasi-equilibrium regime with no quick removal of solvent (water), at ambient or elevated temperatures, under quick solvent evaporation, *etc*.[30] Sol–gel methods are traditionally used for the synthesis of metal oxides because they enable the formation of oxo bridges by hydrolysis and polycondensation of precursors in the presence of water[42–49] or by the sol–gel process using water formed *in situ*;[49–54] a non-hydrolytic process[45,55] is also possible (in this case, oxygen comes from oxygen-containing compounds, *e.g*., ethers, alcohols, alkoxides, *etc*.).

Various combinations of 'wet' chemistry methods are widely used to prepare bimetallic nanoalloys representing the active components of catalysts for important catalytic processes, *e.g*., generation of hydrogen.[56–61] Undoubtedly, these methods offer great prospects for the design of bimetallic catalysts of versatile compositions with different structural types of their surfaces and enable controlled improvement of catalytic properties.

2. The structure of bimetallic nanoalloys

The structure of bimetallic nanoalloys depends on the thermodynamic properties of the starting system.[17] Publications in the field of catalysis concern four structural types of bimetallic nanomaterials depending on the type of atomic mixing:

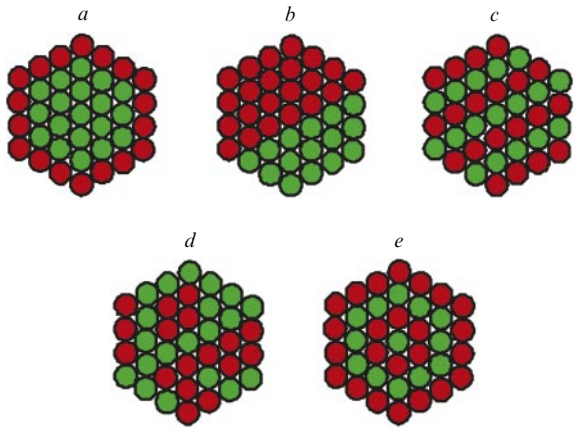


Figure 1. Cross-sections of bimetallic particles: core–shell alloy (*a*); nanoalloy with separation on the atomic level (*b*); nanoalloy with ordered metal atoms (*c*); nanoalloy with randomly disordered metal atoms (*d*); and onion-type alloy (*e*).

— core–shell structures where a monometallic core is coated with a different-metal shell (Fig. 1 *a*); materials with this structural type are not infrequent to occur;[19]

— nanoalloys separated on the subcluster level form if two metallic components are separated by a pseudoflat surface (Fig. 1 *b*); this structural type is very rare to occur;[21,22]

— homogeneous nanoalloys formed by mixing two metals; their atoms can be ordered (Fig. 1 *c*) or randomly distributed (Fig. 1 *d*); disordered nanoalloys are more often to occur in catalysis than ordered nanoalloys;[61–65]

— multishell nanoalloys, or onion-type structures, represent systems where the metal core is surrounded by a number of concentric shells (Fig. 1 *e*).

The structures of a number of bi- and trimetallic nanoalloys have been studied.[66,67] Prerequisites for particular structural types have been analyzed.[21] We believe that understanding and prediction of a particular structure of a nanoalloy requires a thorough examination of published data on physicochemical analysis and taking into account the fact that most catalytic reactions in question proceed at moderate temperatures.

3. Main methods for qualitative and quantitative analysis of catalyst surfaces

The rates of formation of different products of a multistep catalytic reaction are determined by different active sites on the catalyst surface. That is why heterogeneous catalysts are prepared in the form of nanoparticles with high concentration of surface active sites (see above). The design of nanosized new-generation catalysts is immediately related to progress in physical methods of investigation of surface that help to identify and characterize the surface active sites on the atomic level.[68] Usually, various combinations of different methods are used because studies on nanosized systems require high accuracy of determination of geometric parameters and chemical properties of materials. When studying synergistic effects in reactions on bimetallic nanoalloys, the possibility of investigating structural transformations *in situ* is of particular importance. Now we will briefly outline the physical methods that are most often

used to analyze the structure of nanosized materials (particular properties to be studied are listed in parentheses):

— transmission electron microscopy (size, shape, surface crystallinity);

— scanning electron microscopy (size, surface relief);

— atomic force microscopy (size, surface relief);

— scanning tunnelling microscopy (size, surface relief, conductivity);

— X-ray powder diffraction (crystallinity, phase composition in the bulk);

— small-angle X-ray scattering (phase composition, size distribution of phase inhomogeneities in the bulk);

— X-ray photoelectron spectroscopy (binding energy of electrons, oxidation state, size, chemical composition of surface);

— X-ray emission spectroscopy (band gap, electron energy band structure, distribution of the density of states for valence electrons);

— X-ray spectroscopy NEXAFS§ (qualitative and quantitative compositions in the bulk, coordination numbers);

— X-ray spectroscopy EXAFS§ (local environment of atoms of constituent elements);

— X-ray spectroscopy XANES§ (investigations of X-ray absorption near-edge structure);

— UV spectroscopy (absorption, emission, optical reflection, size);

— IR spectroscopy of adsorbed probe molecules, CO and C_5H_5N (qualitative and quantitative compositions of surface adsorption sites);

— photoluminescence spectroscopy (refractive index, absorptance, quantum yield);

— Mössbauer spectroscopy (phase composition, local environment of atoms, size);

— atomic absorption spectroscopy (qualitative and quantitative compositions of samples of various materials);

— chemisorption of probe molecules, H_2 and O_2 (qualitative and quantitative compositions of surface adsorption sites);

— temperature programmed reduction or oxidation (phase composition, oxidation states of metals on the surface of materials);

— thermal desorption of inert molecules, N_2, He and Ar (surface areas);

— gas-liquid chromatography (adsorption properties of surfaces);

— energy dispersive X-ray analysis (chemical composition of surface);

— electron paramagnetic resonance (chemical composition in the bulk);

— density functional computational method (structure, shape, adsorption and chemical properties of surface).

III. Bimetallic nanoalloys in selective hydrogenation of hydrocarbons

1. Raney nickel

In spite of considerable progress in physical methods, theoretical approaches and computer technologies, studies on the properties of catalysts as well as search for novel high-performance materials are still based on the knowledge about the available catalysts. Moreover, recent studies revealed a great potential for improvement of the catalytic properties of these catalysts and their analogues.

Raney nickel, a nickel–aluminium alloy, is a well-known and widely used catalyst for hydrogenation of unsaturated organic compounds.[69] It is utilized in such large-scale processes, as the synthesis of intermediate monomers for production of nylon and urethanes, as well as in production of sorbitol, a key component of many drugs and chemicals. Wide use of Raney nickel is also due to optimum ratio of the key parameters, *viz.*, activity and cost. The catalyst has porous structure and is obtained by aluminium leaching from the starting nickel–aluminium alloy. High hydrogenating activity is simultaneously an advantage and a drawback of the catalyst (in some cases, organic synthesis of complex molecules requires hydrogenation of particular unsaturated groups while other groups should remain untouched).

a. Modification of Raney nickel by quenching

It was proposed [70] to modify the synthesis of Raney skeletal catalyst in order to enhance its selectivity using quenching upon melting of main components.[71–73] The structural parameters and catalytic properties of the rapidly quenched catalyst (RQ Ni) were compared with those of untreated (standard) Raney nickel.[74–79] Using elemental analysis, adsorption of nitrogen, scanning electron microscopy, X-ray powder diffraction and hydrogen desorption, it was established that the skeletal catalyst prepared by leaching from rapidly quenched alloy $Ni_{50}Al_{50}$, differs from standard Raney nickel in phase composition, particle size, surface area and porosity. A thorough examination of X-ray powder diffraction data showed that the crystallite size and the lattice constant of RQ Ni are larger than those of standard Raney nickel. The main difference of the modified catalyst is that it is characterized by one peak in the H_2 desorption profile at higher temperatures (>520 °C) in contrast to the standard catalyst characterized by two peaks in the H_2 desorption profile in the temperature range from 400 to 520 °C.

Tentative conclusions on the reasons for differences in the catalytic properties of these catalysts are as follows. A comparison of the results of catalytic tests showed [70] that RQ Ni exhibits much higher activity and selectivity to particular products of hydrogenation or has at least identical selectivity as the industrial catalyst. Significant improvement of catalytic properties can be explained by defectiveness of large crystallites and by the pore size in RQ Ni. Stabilization of the skeleton and inhibition of pore collapse in RQ Ni are due to the appearance of the intermetallic phase Ni_2Al_3 as a result of rapid quenching of the nickel–aluminium alloy.[80] Hydrogen desorbed at lower and at higher temperatures was treated in different manner, namely, as 'weakly bound' and 'strongly bound' to the structure of the molten catalyst, respectively.

It was found that the new system is a selective catalyst for hydrogenation of functional groups in a large number of organic substrates including aromatics in which the aromatic nucleus remains untouched. This means that the active sites on RQ Ni act 'more concertedly' in respect to delivery of active hydrogen to functional groups. Correlations between the bond energy of chemisorbed hydrogen

§ NEXAFS stands for Near Edge X-ray Absorption Fine Structure, EXAFS stands for Extended X-ray Absorption Fine Structure and XANES stands for X-ray Absorption Near Edge Structure.

and the activity and selectivity of catalysts for some reactions were reported.[81–84] In particular, it was shown that the selectivity of hydrogenation of 2-ethylanthraquinone is governed by the relative amounts of the weakly and strongly bound hydrogen[84] because the weakly bound hydrogen is highly active in the hydrogenation of aromatic ring, while hydrogenation of carbonyl groups is determined by the electronic mechanism and is limited by the activation of hydrogen.[85] It is believed[70] that RQ Ni can be a promising alternative catalyst for the key reaction of selective hydrogenation of 2-ethylanthraquinone to produce hydrogen peroxide.

There exist convincing proofs[86] that a catalyst based on the intermetallic compound $Fe_{0.95}TiZr_{0.3}Mo_{0.2}$ can accumulate hydrogen. It was found that adsorption is accompanied by uptake of 2 mol of H_2 of which 1.82 mol can be desorbed with ease at 300–350 °C. Hydrogenation of CO_2 in the presence of this system proceeds nonselectively and affords up to 30% of methane. However, the addition of hydride $[Fe_{0.95}TiZr_{0.3}Mo_{0.2}]H_{0.18}$ containing strongly bound hydrogen to the catalyst causes initiation of selective hydrogenation of CO_2 into CO at room temperature. At 450 °C, the selectivity of the catalyst in the formation of carbon monoxide was 99% at a CO_2 conversion of 50%.[87–89]

b. Modification of Raney nickel with palladium or platinum

In a number of catalytic applications, Raney nickel is competitive with supported palladium and platinum in respect to cost/activity ratio (Pd and Pt catalysts are about 100 times more expensive than nickel but have higher specific activities). Catalysts based on noble metals should meet the following additional requirements:

— have sufficiently long lifetimes in some particularly valuable organic syntheses; and

— undergo full reduction if necessary.

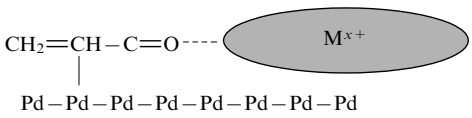
Schmidt[90] attempted to enhance the catalytic activity of Raney nickel in order to make it a cheaper and competitive alternative to the supported catalysts Pd/C or Pt/C through an increase in the lifetime and the ability to function in a wide range of operating conditions, especially at low pressures. Very small amounts of precious metal (PM) were deposited on the Raney catalyst surface (from this point on, PM/Ni) by impregnation from solution. It was assumed that the PM ion will be reduced with nickel or with the surface hydrogen to avoid further activation or reduction of the PM.

The reductive abilities of Raney nickel and adsorbed hydrogen were also utilized for modification using molybdates as promoters.[91] The synthetic procedure involved the use of basic salts of palladium or platinum (amino complexes) as the key step. The results obtained were compared with those obtained for materials synthesized earlier in this research group by impregnation the Raney nickel catalyst with acidic salts of noble metals. Results of elemental analysis of the surface (obtained by X-ray photoelectron spectroscopy[90]) and catalytic tests in the hydrogenation of *p*-nitrotoluene[92] are available. Tests showed that the results of selective hydrogenation in the presence of catalysts prepared with basic salts of platinum and palladium were better than the results obtained in the presence of catalysts based on acidic salts. In turn, both PM/Ni catalysts of hydrogenation in a stationary reactor showed much higher turnover number than the standard Raney nickel with very low amount of Pd (only 0.25% *vs.* 1%–5% for Pd/Al_2O_3 and Pd/C). In the PM/Ni catalysts, the content of PM was about 1 atom per 700 Ni atoms. The same amount of palladium on an alumina support showed no activity at all. It was assumed[92] that the synergistic effect is due to spillover of excess hydrogen supplied from the bulk of nickel to the surface sites containing palladium and contacting the substrate.

2. Catalysts based on palladium nanoalloys

Generally, the promotion of monometallic palladium catalysts by adding the second metal can be explained by the following factors: geometric and electronic effects, appearance of mixed active sites and a decrease in the starting metal–hydrogen bond energy. Some reaction classes are to a greater or lesser extent sensitive to these factors.[93] For instance, electronic effects play a decisive role in selective hydrogenation of unsaturated hydrocarbons, geometric aspects dominate in the hydrogenolysis of alkanes, while the appearance of mixed active sites governs selective hydrogenation of α,β-unsaturated aldehydes into unsaturated alcohols. In other words, explanation of the influence of the second metal on the properties of palladium is reaction dependent. The presence of an oxide in the palladium alloy usually promotes the synergistic effect that manifests itself as enhancement of catalytic activity in the selective hydrogenation of, *e.g.*, a carbonyl group bonded to the carbon–carbon multiple bond.[93,94] In this case, the active centre can be described as $Pd-M^{x+}$ and activation of the C=O bond in α,β-unsaturated aldehydes on these active centres can schematically be represented as follows:

Scheme 1



M = Sn, Ge, Fe, *etc.*

Synergistic effect in selective hydrogenation of carbonyl group in α,β-unsaturated aldehydes is due to close approach of two active centres, a positively charged ion M^{x+}, which activates the C=O bond, and the palladium atom bearing chemisorbed hydrogen. By and large, the mechanism of the synergistic effect is very similar to the mechanism of the catalytic effect owing to strong metal–support interaction.[95,96]

The appearance of a modifier on the surface and in the bulk influences the relative strength of adsorption of alkynes (or alkadienes) and alkenes, which leads to an increase in the reactivity of alkynes and a decrease in that of alkenes. The geometric effect emerging upon dilution of the palladium surface layer makes the intermediate formation of alkylidenes less probable. Enhancement of catalytic activity towards styrene hydrogenation into ethylbenzene and an increase in stability to sulfur present in the reactant was observed after adding cobalt and tungsten to Pd/Al_2O_3.[97] This was explained by the formation of highly active mixed centres Pd–Co and Pd–W. At the same time, the addition of platinum to palladium supported on pumice produced a negative effect in selective hydrogenation of cycloocta-1,3-diene into cyclooctene.[98,99]

Examples of discussion of the influence of the second metal on the catalytic properties of palladium in the hydrogenation of aromatic, nitrogen-containing and aliphatic compounds can be found, in particular, in Ref. 93.

3. Role of quantum chemical calculations in the design of catalysts for hydrogenation

Palladium–silver bimetallic nanoalloys are widely used as catalysts of selective hydrogenation.[100–102] To explain the mechanism of sorption/desorption of reactants (H, CO, *etc.*) on the surface of nanosized catalysts based on bimetallic alloys in the course of reaction, one should know the nature of chemical bonding between metal atoms and adsorbents and take into account the stability conditions for different types of nanosized structures. Theoretical calculations are a key source of information in this field.[103, 104]

Publication of the breakthrough studies on the molecular design of high-performance nanosized catalysts[105–109] became possible due to the development of the first-principle (*ab initio*) computational methods[103] that use the density functional theory, to the cluster approach,[104] which allows one to include nonstoichiometry of intermetallics and the local disorder effects typical of nanoparticles. It was shown[110] that preparation of high-performance catalysts that are based on non-noble metal alloys and can compete with the Pd–Ag catalyst[100–102] is not improbable.

Comparative density functional calculations of the optimal geometry and electronic structure of clusters of various metals revealed promising catalysts for hydrogenation of acetylene, namely, intermetallics of the Ni–Zn system. Taking into account the results obtained, a catalyst based on Ni_1Zn_3 alloy with preset properties (in particular, high selectivity in the reaction of partial hydrogenation of acetylene) was synthesized.[110] Nickel–zinc alloys with a Zn content from 45% to 75% synthesized on $MgAl_2O_4$ support were tested in the hydrogenation of acetylene. The results of comparative catalytic tests are presented in Fig. 2.¶

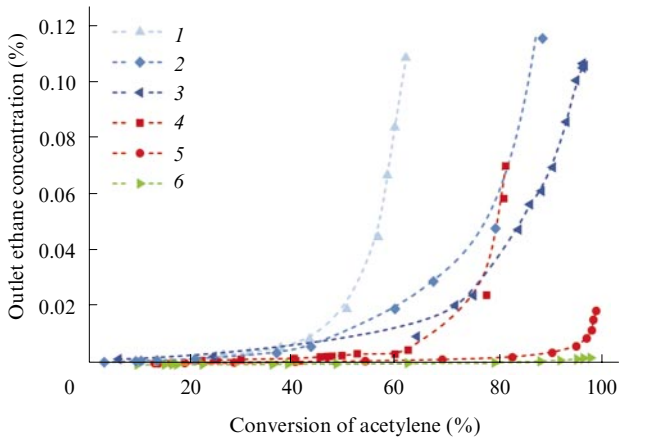


Figure 2. Ethane concentration at the reactor outlet plotted *vs.* conversion of acetylene for different catalysts.[110]
Catalyst: 100% Ni (*1*), 45% Ni + 55% Zn (*2*), 33% Ni + 67% Zn (*3*), 100% Pd (*4*), 25% Pd + 75% Ag (*5*), and 25% Ni + 75% Zn (*6*).

4. Role of promoters in bimetallic catalysts

A drawback of Pd-based catalysts traditionally used in selective hydrogenation of hydrocarbons consists in low selectivity, in particular, in the conversion of acetylene to ethylene.[111–113] It can be eliminated by appropriately choosing the second metal to form the nanoalloy or Pd-based cluster structures.[114–116]

a. Segregation phenomena and the local composition of palladium alloys

The appearance of a modifier on the surface and in the bulk causes changes in the geometry and electronic structure of the surface and in the near-surface layers of a bimetallic alloy including segregation of the modifier on the surface. The segregation energy (difference between the calculated total free energy of the surface atoms and the energy of atoms in the bulk of the catalyst) depends on many factors including position of the replaced atom on the surface, atomic radius and the surface energy of the metal.[108, 117–119]

Segregation is immediately related to changes in the relative strength of adsorption of intermediate reactants (adsorbates) on the surface. Thus, the design of nanosized bimetallic catalysts with improved properties requires taking account of the influence of segregation on the local compositions of the catalysts. It is known that the composition of the clean surface of disordered binary alloys $Pd_{1-x}Ag_x$ is significantly different from the composition in the bulk owing to strong surface segregation of silver. In particular, scanning electron microscopy studies of a $Pd_{0.67}Ag_{0.33}$ single crystal annealed at 720 K showed that only 5% of atoms on the (111) face represent palladium atoms.[120, 121] Similar results were also reported in other studies.[107, 108, 122, 123]

Density functional theory quantum chemical calculations[107–109] confirmed that silver atoms are prone to surface segregation and gave an explanation for this phenomenon. Also, the relative segregation energies of Ag atoms were calculated for different models of the surface of Pd–Ag binary alloys including the Pd(111), $Pd_{0.75}Ag_{0.25}$(111), $Pd_{0.5}Ag_{0.5}$ (111) and Ag(111) faces; restructuring of the surface with adsorbates was ignored.

However, the key structural and therefore, electronic parameters of the surface of Pd–Ag alloys can vary over a wide range in the presence of adsorbates. For instance, re-segregation of Ag from the surface of $Pd_{0.75}Ag_{0.25}$ membranes at high pressure of hydrogen was detected by X-ray photoelectron spectroscopy.[124] Based on the fact that the Pd–H bond is stronger than the Ag–H bond, it was assumed[116] that hydrogen consumed in the hydrogenation of acetylene influences the composition of the surface structures in the Pd–Ag system in such a manner that the surface concentration of palladium increases. This plays an important role in complex interaction of the surface (and subsurface) of palladium catalysts with hydrogen in the course of hydrogenation.[125, 126] The structure of the surface of $Pd_{1-x}Ag_x$ materials interacting and not interacting with hydrogen was studied, with the emphasis placed on the

¶ The amount of ethane is a measure of selectivity in the hydrogenation of acetylene; the smaller the amount of ethane the higher the selectivity of the reaction.

promoting role of silver in the selective hydrogenation on Pd–Ag catalysts.[109,127] Models and computational methods were described. The local composition and possible structures of the clean surface of $Pd_{1-x}Ag_x$ with different local symmetry and the surface with adsorbed hydrogen were discussed. The problem of re-segregation in bimetallic materials, due to the presence of reactants that mainly react with a particular component was considered. It was emphasized that the problem is of great importance for various materials based on bi- and polymetallic systems, being closely related to the interaction of hydrogen atoms on the alloy surface. Hydrogen atoms present on bimetallic surfaces $Pd_{1-x}Ag_x$ under the conditions of hydrogenation reaction mainly react with the active sites comprising the largest number of palladium atoms and avoid the active sites comprised of silver atoms.

Thus, the necessary restructuring of the surface of $Pd_{1-x}Ag_x$ materials should be accompanied by an increase in the number of hydrogen atoms adsorbed on the surface. The results of calculations of the energies of the interaction between H atoms and the surface[109] confirm changes in the surface structure and provide an illustration for a more general statement, according to which the properties of the surface of bimetallic systems are governed by so-called ensembles of particles.[17,128] In other words, the interaction of substrates with adsorption sites depends solely on the structure and composition of the nearest environment of these sites.[118,129–133]

Adsorbed hydrogen atoms dramatically change the ability of silver experience segregation, *viz*., an increase in the amount of hydrogen initiates re-segregation of silver atoms from the surface.[109] At sufficiently high coverages with hydrogen, the surface layer can contain mainly palladium atoms. The activation energies for diffusion of hydrogen were calculated using the model system $Pd_{0.8}Ag_{0.2}(111)$ at different surface (subsurface) compositions assuming a low content of hydrogen. On the surface with segregated silver atoms, displacements of adsorbed hydrogen atoms from their positions in the f.c.c. lattice ($Pd_3–Ag_3$) to the defect near-surface layer is energetically favourable and indicates that the subsurface can be stabilized with hydrogen. If the initial surface layer contains only palladium atoms, all silver atoms being in the near-surface layer, adsorbed hydrogen atoms spontaneously (barrierlessly) leave both octahedral ($Pd_3–Ag_3$) and tetrahedral ($Pd_3–Ag_1$) sites and diffuse towards the alloy surface. The results obtained in Ref. 109 confirm the hypothesis that silver atoms in the near-surface layer in the presence of excess hydrogen suppress the appearance of near-surface hydrogen and, therefore, preclude full hydrogenation of unsaturated hydrocarbons. The phenomena considered in that study are closely related to the promoting properties of one component of bimetallic materials and can be applied to diverse processes occurring on the surface of various substrates including hydrogenation reactions on $Pd_{1-x}Ag_x$ catalysts.

b. Catalyst of selective hydrogenation based on Pd–Zn nanoalloy

Bimetallic catalysts based on Pd–Zn nanoalloy deserve particular attention since they are successfully used in industrial processes, *e.g*., selective hydrogenation of acetylene hydrocarbons,[14,27] steam reforming of methanol,[131] and in the conversion of biomass into hydrocarbon fuel components.[132] A recent review[131] includes a detailed analysis of methods of formation of Pd–Zn catalysts based on organic and inorganic precursors as well as metallurgical methods for preparation of Pd–Zn alloys at elevated temperatures.

Studies on the influence of morphology of bimetallic catalysts on their activity are rapidly progressing now. They are related to structure–activity relationships that are to one or another extent discussed in the literature.[11,14,27,30–32] The authors of this review believe that morphological features do not always affect correlations

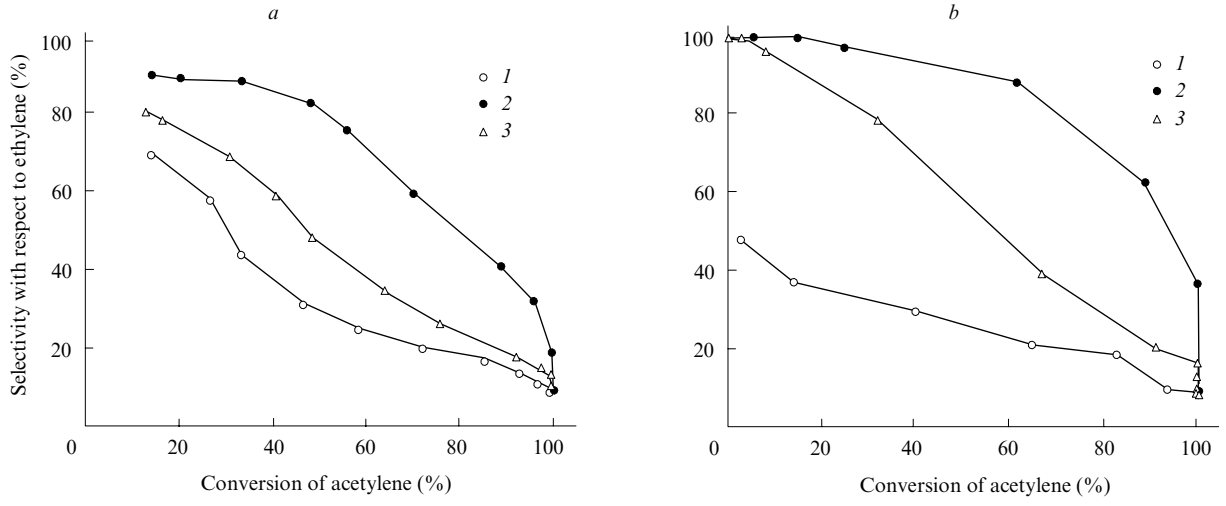


Figure 3. Selectivity with respect to ethylene plotted *vs*. conversion of acetylene in the hydrogenation of acetylene.[134]
(*a*) High-grade catalysts: (*1*) 0.93% Pd/Al_2O_3, obtained by impregnation from $Pd_3(OAc)_6$; (*2*) 0.93% Pd + 0.58% Zn/Al_2O_3, obtained by impregnation from $PdZn(OAc)_4 \cdot H_2O$; (*3*) 0.93% Pd + 0.58% Zn/Al_2O_3, obtained by impregnation from $Pd_3(OAc)_6 + Zn(OAc)_2 \cdot 2H_2O$. (*b*) Low-grade catalysts: (*1*) 0.04% Pd/Al_2O_3, obtained by impregnation from $Pd_3(OAc)_6$; (*2*) 0.04% Pd + 0.025% Zn/Al_2O_3, obtained by impregnation from $Pd + Zn(OAc)_4 \cdot H_2O$; (*3*) 0.04% Pd + 0.025% Zn/Al_2O_3, obtained by impregnation from $Pd_3(OAc)_6 + Zn(OAc)_2 \cdot 2H_2O$.

between the structure and catalytic properties and that this undoubtedly important field of studies on the active surface of catalytic systems still requires a thorough analysis and reasoning.

The activity of supported catalysts to a great extent depends on the method used for the synthesis and, in particular, on the nature of precursors. In this connection, catalytic systems Pd–Zn prepared by different methods and tested in the selective hydrogenation of acetylene (Fig. 3) are of interest. They were prepared from the heterobimetallic acetate complex $PdZn(\mu\text{-}OAc)_4 \cdot H_2O$ as precursor.[134, 135] Using X-ray power diffraction and EXAFS, it was found that reductive activation of this complex supported on alumina in H_2 atmosphere leads to formation of a Pd–Zn alloy that provides enhanced selectivity of the $Pd-Zn/Al_2O_3$ catalyst.[134]

The catalytic system $Pd-Zn/Al_2O_3$ prepared from the heterobimetallic complex exhibits the best operating characteristics compared to those of the same-composition catalyst prepared from a mixture of metal complexes and the catalysts containing monometallic active components (see Fig. 3).

The surface structure of Pd–Zn alloy and its electronic structure were analyzed by the density functional theory method.[136–138] The results obtained may help in understanding the nature of the reduced hydrogenating activity and simultaneously high selectivity in the partial hydrogenation of the triple to double carbon–carbon bond on the Pd–Zn catalyst.

c. Catalyst for selective hydrogenation based on Au–Ag nanoalloy

Pioneering studies[139, 140] on gold-containing supported catalysts aroused huge interest of researchers. These catalysts are widely used in selective hydrogenation of hydrocarbons.[141–143] The selectivity of hydrogenation of acetylene on the gold-containing catalysts is very high because of the unique situation, namely, the adsorption capacity of gold with respect to acetylene is higher than to alkenes.[33, 144] However, conversion at low temperatures is low.[145, 146] The catalytic characteristics of gold depend on the particle size; the optimal Au particle size is $\sim$3 nm.[147]

The selectivity of the $Au-Ag/SiO_2$ catalyst was for the first time studied taking hydrogenation of acetylene in excess ethylene as an example.[148] It should be noted that silver was not thought to be a good candidate for improvement of acetylene conversion in this reaction despite the fact that preferred oxidation of CO in hydrogen atmosphere in the presence of Au–Ag alloy was accompanied by strong synergistic effect.[149] Gold and silver were reduced using two-step impregnation on the silica surface treated with 3-aminopropyltriethoxysilane (APTES) following a known procedure.[149, 150] This led to formation of very small particles of the Au–Ag alloy. APTES was removed by cold plasma treatment under mild conditions. The size of Au–Ag bimetallic particles was determined by X-ray power diffraction and transmission electron microscopy. The X-ray diffraction patterns of the dried, annealed at high temperature, and cold plasma treated samples of the $Au-Ag/SiO_2$ catalyst were compared. The corresponding average microcrystallite size appeared to be 2.2, 2.9 and 2.8 nm. After reduction of the samples at 250 and 400 °C, X-ray reflections remained broadened and the average particle size varied within the limits of measuring error. Transmission electron microscopy data almost coincided with the results obtained by X-ray power diffraction, thus confirming the conclusion[149, 150] that silver stabilizes nanoparticles and prevents them from sintering in the course of high-temperature annealing.

Since metallic gold and silver have identical f.c.c. lattices, their X-ray diffraction patterns almost match each other.[130] The formation of 3-nm Au–Ag structures in the active component was established by UV spectroscopy.[151–153] The spectra of Au–Ag alloy nanoparticles calculated using the Mie scattering theory (see Refs 151 and 154–156) matched the experimental UV spectra.

The UV spectra of the $Au-Ag/SiO_2$ samples annealed and reduced at 250 °C revealed a shift of the peak corresponding to absorption of gold particles towards that of monometallic silver. This indicates that the surface of nanoparticles is enriched with silver.[149, 150, 152, 157] According to a correlation of the composition of the Au–Ag system (see Ref. 152), the maximal gold content (68 mass %) is close to the value determined by inductively coupled plasma mass spectrometry (66 mass %). Based on the aforesaid, it was concluded that the Au–Ag bimetallic particles reduced at 250 °C represent disordered alloys. Enrichment of the surface of gold particles with silver to 57% causes no changes in the structure of the disordered alloy. Clearly, melting stabilizes Ag^0 atoms in the Au–Ag nanoparticles, thus precluding their oxidation.

Catalytic tests showed that acetylene conversion on the plasma-pretreated $Au-Ag/SiO_2$ catalyst was much higher than on the sample annealed at 500 °C, although the latter contains particles of the same size. Plasma treatment enhances the activity of catalysts irrespective of the particle size. Probably, it also leads to strong interaction between nanoparticles of Au–Ag alloy and the SiO_2 support and to subsequent improvement of catalytic properties.

It should be emphasized that the addition of silver to gold-containing catalysts enhances not only the selectivity with respect to ethylene, but also the conversion of acetylene. This differs from the results obtained on Pd–Ag catalysts for which the addition of silver is usually followed by enhancement of selectivity and reduction of the conversion of acetylene.[142, 158] The aforesaid shows that the mechanisms of the selective hydrogenation of acetylene in excess ethylene on gold-containing catalysts and on palladium systems are different.

The results of experiments on conversion on Au/SiO_2 and $Au-Ag/SiO_2$ samples reduced at 400 °C as well as their selectivities were also reported.[148] In this case, Au/SiO_2 showed a much lower activity while the conversion was $< 1\%$ in the temperature range 150–250 °C. Therefore, the activity of the annealed Au/SiO_2 is sensitive to the reduction conditions, and reduction at high temperatures is deteriorative to the gold-containing supported catalysts in the hydrogenation of acetylene. The catalytic activity of $Au-Ag/SiO_2$ reduced at 400 °C was also lower than that of the sample reduced at 250 °C, but the selectivity increased to 99% in the whole temperature range.

IV. Bimetallic nanoalloys in the oxidation of CO in hydrogen atmosphere

Reactions involving oxygen transfer in the presence of gold-containing catalysts[159] at room temperature and, in particular, catalytic oxidation of CO in hydrogen atmosphere,

attract considerable attention and are intensively studied in connection with great importance of these processes for basic research and for industrial applications, such as air cleaning,[160, 161] afterburn of engine exhaust gases,[162–164] and removal of trace amounts of carbon monoxide present in hydrogen on proton-conducting membranes in fuel cells.[165–169] Complication of the last-mentioned process consists in the need to achieve a high reaction rate with simultaneous maintenance of very high selectivity with respect to CO oxidation. The catalytic activity in this reaction is sensitive to Au particle size, the nature of support and to methods of synthesis.[170]

The key step in the oxidation of CO is activation of oxygen.[171] Gold nanoparticles are characterized by good adsorption of CO molecules but they poorly activate and weakly adsorb oxygen molecules.[172, 173] As a result, an important role in the activation of oxygen is often played by the oxide support. It was assumed [171, 174] that in this case, active sites occupy the gold/oxide contact surface. Indeed, most active gold-containing catalysts represent active supports (TiO_2, Fe_2O_3, *etc.*) coated with nearly 3-nm gold particles. An alternative route to active catalysts of CO oxidation is to dope Au particles with a second metal having more pronounced reductive properties. In this case, an increased adsorption of CO causes more intense electron transfer to oxygen. High activity of Au_nSr clusters in this reaction was reported.[159, 175] However, 'soft-landing' on MgO is inappropriate for production of the necessary amounts of the catalyst. There is considerable literature on the catalytic oxidation of CO on monometallic nanoparticles, but corresponding experimental studies using bimetallic particles are few. The most important investigations were analyzed in a review.[32]

1. Catalysts based on Au–Ag nanoalloy

Mou and co-workers described the first bimetallic nanosized catalysts for the oxidation of CO and reported a series of studies [149, 150, 152, 176, 177] on the synergistic effect in this reaction on Au–Ag alloys. They paid considerable attention to the structural organization of the active components. The Au–Ag catalysts were synthesized in the form of alloy nanoparticles supported on mesoporous aluminosilicate (MCM) by the known one-step method.[178, 179] A solution of hexadecyltrimethylammonium bromide was used as stabilizing agent for nanoparticle and the template for the formation of mesoporous structure. UV spectroscopy data revealed the formation of Au–Ag alloy nanoparticles that were larger than Au particles (more than 30 nm *vs.* about 6.7 nm, respectively) and demonstrated much higher catalytic activity in the oxidation of CO. Therefore, the particle size does not play the decisive role for catalytic activity. The activity varies depending on the gold : silver molar ratio, the highest conversion is achieved at an Au : Ag ratio of 3 : 1 and the rate of the reaction can be as high as 8.7×10^{-6} mol (g of catalyst)$^{-1}$ s^{-1} even at negative temperatures (−23 °C). It is believed that strong synergistic effect of co-adsorption of CO and O_2 on Au–Ag particles is the key feature in the catalytic reaction.[176, 177, 180]

Nanoparticles of Au–Ag alloy 4–6 nm in size were synthesized by the two-step method using APTES.[149, 150] They showed high catalytic activity and stability in the low-temperature oxidation of CO. Also, the catalyst is moisture-resistant on long-term storage. The activity of the catalyst depends on its composition, the optimal activity was achieved at an Au : Ag ratio of 3 : 1. The scheme of synthesis of Au–Ag nanoalloy particles supported on SiO_2 was reported by Zhang and co-workers.[149] The samples synthesized were characterized using known procedures.[181–183] Based on experimental UV spectroscopy data[184] and on the results of density functional calculations of a series of model clusters, it was shown [149] that during the synthesis the Ag^+ cations are mainly adsorbed on the surface of the negatively charged gold particles rather than on free amino groups. Also, after reduction, Ag ions adsorbed on the surface of gold particles form a shell representing an individual phase.[185, 186] Silver atoms contacting the surface of Au particles diffuse into the interior, thus forming the Au–Ag alloy. On further annealing in air at 500 °C, the silver shell is oxidized and silver segregation on the surface of the core Au–Ag alloy occurs simultaneously.[109, 176] It should be emphasized that particles are not sintered, probably due to the effect of the oxide film on the surface, which acts as 'glue' between the silica support and the core of the alloy. Final calcination at 550 °C in hydrogen atmosphere involves reduction of a thin AgO layer and re-melting of gold and silver, which activates the catalyst.

The Au–Ag alloys thus synthesized have much smaller particles size compared to monometallic catalysts. Because of this, and owing to the promoting role of silver in the activation of oxygen, they demonstrate improved catalytic properties in the oxidation of CO even in hydrogen-rich atmosphere. The results of catalytic tests for Au–Ag/SiO_2 are presented in Figs 4 and 5. From Fig. 4 it follows that the Au–Ag/SiO_2 catalysts are active in the oxidation of CO even at −50 °C and exhibit much better properties than the Au/TiO_2 reference catalyst from World Gold Council.

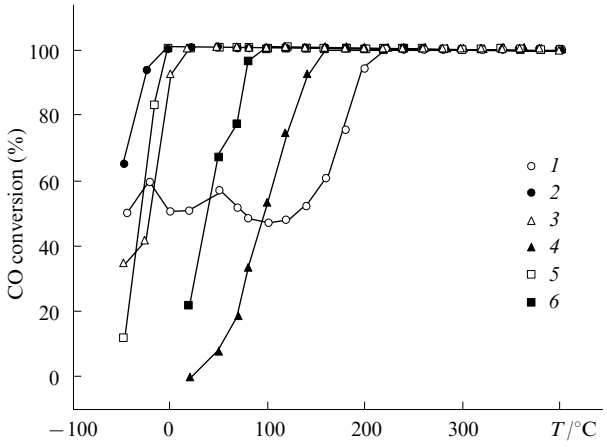


Figure 4. Plots of CO conversion *vs.* reaction temperature over Au–Ag/SiO_2 catalysts with a common metal content of 6 mass % and different Au : Ag ratios (*1–4*) and over K1 and K2 catalysts (*5*, *6*).[149]

Catalysts Au–Ag/SiO_2: pure gold (*1*), Au : Ag = 3 : 1 (*2*), 1 : 1 (*3*); pure silver (*4*). Catalyst K1 — Au/TiO_2 (provided by the World Gold Council; 1 mass % Au, no pretreatment), K2 — Au/TiO_2 (provided by the World Gold Council; 1 mass % Au, calcination at 500 °C for 6 h followed by reduction at 550 °C for 1 h).

Reaction mixture composition (vol.%): CO : O_2 : He = 1 : 1 : 98; flow rate: 20 ml min^{-1}. In each experiment, 60 mg of the catalyst was used.

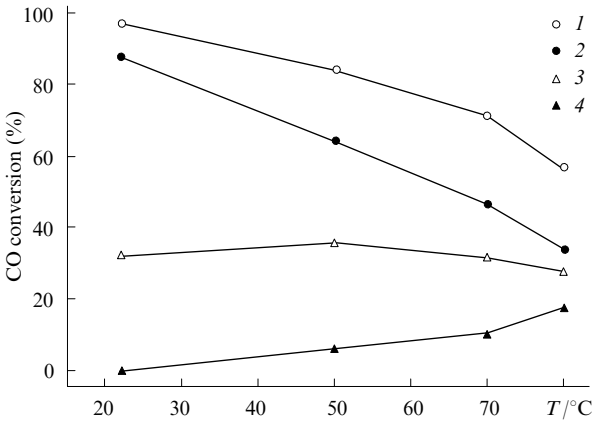


Figure 5. Plots of CO conversion *vs.* reaction temperature over $Au-Ag/SiO_2$ catalysts with a common metal content of 6 mass% and different Au : Ag ratios.[149]
Au : Ag = 1 : 1 (*1*), 3 : 1 (*2*); pure gold (*3*), pure silver (*4*). Reaction mixture composition (vol.%): $CO : O_2 : H_2 : He = 1 : 0.5 : 50 : 48.5$; flow rate: 40 ml min^{-1}. In each experiment, 60 mg of the catalyst was used.

2. Catalysts of oxidation based on Au–Cu nanoalloy

Nanoparticles of Au–Cu alloy about 3 nm in size were synthesized on SBA-15 supports at a wide range of component ratios (Au : Cu).[61, 187] The catalysts with different gold : copper ratios demonstrated higher activity in the PROX reaction on both supports compared to the monometallic Au catalyst and thus the synergistic effect in catalytic activity. The $Au-Cu/SiO_2$ (Au : Cu = 20 : 1) catalyst was characterized by the highest activity at room temperature while the sample with Au : Cu = 3 : 1 was the best in the PROX reaction among the catalysts studied in Refs 61 and 187. *In situ* studies by X-ray powder diffraction, electron paramagnetic resonance, XANES and other methods clarified the situation with involvement of the active sites of Au–Cu bimetallic catalysts related to changes in their electronic structure in the PROX reaction.[188]

There is considerable literature on the active sites in Au-containing supported catalysts of the oxidation of CO. The following reaction sites were proposed: cationic compounds of gold;[189, 190] bilayer gold clusters comprising from 1 to 10 atoms;[191, 192] and metal oxide representing an interlayer between gold and support.[159] Cationic compounds of gold were found neither in the pretreated nor in the working Au–Cu bimetallic catalysts. Only Au^0 atoms were detected by IR spectroscopy and XANES. Since gold particles were synthesized before deposition of copper by the two-step method described above,[149] it is most probable that the core–shell structure is formed during copper deposition. Initially, a bimetallic particle represents a gold core surrounded by a CuO_x layer or CuO_x particles. After annealing, copper on the surface is oxidized. A scheme of structural changes in the Au–Cu/SBA-15 catalyst under reduction of hydrogen and oxidation of carbon monoxide proposed using the results of *in situ* studies is shown in Fig. 6.

Electron paramagnetic resonance and XANES studies revealed the presence of Cu^{2+} cations in the annealed sample, while examination by X-ray powder diffraction showed the presence of a pure gold phase instead of

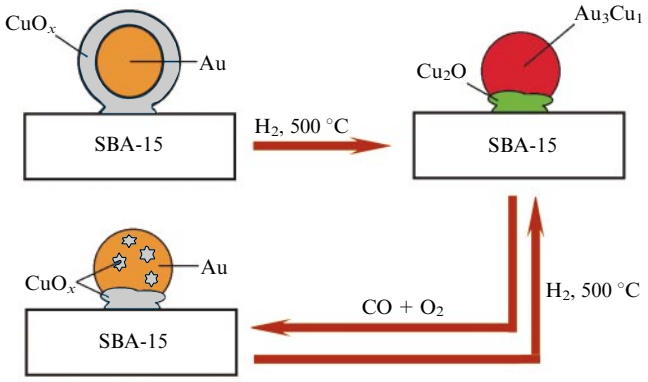


Figure 6. Schematic illustration of structural changes in the Au–Cu/SBA-15 catalyst under H_2 reduction and CO oxidation conditions.[188]

Au–Cu alloy. Heating is accompanied by reduction of copper on the CuO-layer/particles surface to Cu^+ and Cu^0 and diffusion of Cu^0 atoms into the interior of the gold core. This results in the formation of the intermetallic phase Au_3Cu_1 (see Fig. 6); strong interaction of Cu^+ cations with the support limits their mobility and favours agglomeration of particles. When the Au_3Cu_1 phase is exposed to the reaction atmosphere (CO + O_2), Cu^0 in the intermetallic phase is oxidized to Cu^+ and Cu^{2+}; the next surface segregation of copper is followed by the formation of the gold core–CuO_x (particles) structure.

IR spectra of CO adsorbed on Au–Cu/SBA-15 were recorded *in situ* at −110 °C. They clearly demonstrate an absorption band at 2108 cm^{-1} with a shoulder at 2125 cm^{-1}. A comparison with the absorption spectra of CO adsorbed on monometallic Au and Cu catalysts suggests that the main absorption band corresponds to CO adsorbed on Au^0 and the shoulder corresponds to CO adsorbed on Cu^0. After introduction of oxygen, the absorption band at 2108 cm^{-1} weakens with time and disappears after 70 min, the band at 2125 cm^{-1} remains unchanged and an intense absorption band of adsorbed CO_2 appears simultaneously in the spectrum. It follows that, similarly to both monometallic (Au/SBA-15) and bimetallic (Au–Cu/SBA-15) catalysts, carbon monoxide adsorbed on Au^0 directly interacted with oxygen to give CO_2 even at as low temperatures as −110 °C; however, carbon monoxide was adsorbed on Cu^+/Cu^{2+} but no oxidation occurred. It was concluded that the active sites of CO oxidation on monometallic (Au) and bimetallic (Au–Cu) catalysts are Au^0 atoms. This conclusion is also confirmed by the fact that the Cu/SBA-15 catalyst is inactive in the oxidation of CO.[61, 187]

What is the reason for the much higher activity of the bimetallic catalyst Au–Cu compared to monometallic Au catalyst? The particle size of the bimetallic catalyst is much smaller than that of the monometallic catalyst owing to stability to sintering that is due to the copper component.[61, 187] It is believed this is a reason for enhanced activity of the Au–Cu catalyst. One more possible reason is that copper compounds are involved in the activation of oxygen. The bimetallic catalyst in question was supported on the inert support SBA-15 that cannot generate oxygen. Nevertheless, it was found that under the reaction conditions, Cu^0 in the bimetallic catalyst is readily oxidized to

Cu^{+} and Cu^{2+}, thus indicating the possibility to activate oxygen on copper centres. In the course of the reaction the structure of the Au–Cu catalyst represents an inverted structure of Au/CuO_x in which CuO_x is supported onto the surface of Au particles. The Au particle size is only 2–3 nm;[187] therefore, one can assume that CuO_x particles should be very small even on the sub-nanometre scale. In this case, the specific surface area of the interlayer between gold and CuO_x will be large, thus favouring acceleration of the reaction on this surface. Thus, copper in the bimetallic catalyst Au–Cu plays a dual role, *viz*., it holds gold particles on the silica support and activates molecular oxygen for subsequent oxidation of CO.

3. Synergistic effect of the catalyst for oxidation based on Ru@Pt nanoparticles

A novel nanosized catalyst comprised of a ruthenium core coated with a shell of Pt atoms (from this point on, a Ru@Pt nanoparticle with a core–shell structure shown in Fig. 7 *a*) was reported.[193] Nanoparticles Ru@Pt were synthesized in a colloid solution of polyvinylpyrrolidone by reduction of $Ru(acac)_3$ (acac is acetylacetonate) with alcohol followed by deposition of platinum from $PtCl_2$ on slow heating to 200 °C. The product of synthesis, 3-nm ruthenium particles, were coated with platinum and added to the colloid solution of $PtCl_2$ and the system was slowly heated to 200 °C. The core–shell structure of Ru@Pt particles was confirmed by transmission electron microscopy, X-ray powder diffraction, X-ray photoelectron spectroscopy and IR spectroscopy. According to X-ray powder diffraction and X-ray photoelectron spectroscopy data, the core representing an amorphous mixture $Ru^{4+} + Ru^{0}$ was coated with a platinum shell. The average particle size of Ru@Pt was 4.1 nm, which lies between the particle size of monometallic ruthenium (3.0 nm) and platinum (6.1 nm).

To compare the catalytic properties of Ru@Pt particles with those of close analogues, nanoparticles of Pt–Ru alloy (Fig. 7 *b*), monometallic platinum and ruthenium and a mechanical mixture Pt + Ru (Fig. 7 *c*–*e*) were synthesized.[193] The activities of the catalysts based on Ru@Pt, PtRu, Pt + Ru, Pt and Ru in the oxidation of CO in hydrogen atmosphere were evaluated from the temperature of full oxidation of CO in the mixture containing 0.1%–0.2% of carbon monoxide, 0.5% of oxygen and 99.3%–99.4% of hydrogen. It was found that in the case of Ru@Pt, the mixture contains no carbon monoxide at 30 °C [*cf*. 85, 93, 170 and >170 °C for the PtRu, (Pt + Ru), Pt and Ru, respectively]. Noteworthy is also a higher selectivity of oxidation on the Ru@Pt catalyst, namely, 80% *vs*. 50% for the best analogue tested (PtRu). An analysis of published data[194–200] showed that in some cases platinum catalysts show even higher selectivity in the oxidation of CO in the presence of hydrogen, but this requires a reducible oxide support to activate oxygen.

To elucidate fundamental reasons for unique reactivity of bimetallic core–shell nanoparticles Ru@Pt, periodic self-consistent density functional theory calculations were carried out.[193] To compare the reactivities of Ru@Pt and platinum nanoparticles, the binding energies of different intermediates and the activation energy barriers were calculated for elementary steps characterizing the oxidation of carbon monoxide and hydrogen on a number of model surfaces.

A platinum monolayer deposited on a ruthenium support is laterally compressed compared with the lattice constant in the bulk of platinum particle, This can lead to weakening of the interaction of adsorbates on the surface platinum atoms in the Ru@Pt nanoparticles.[201] In addition, the interaction of platinum atoms with ruthenium support atoms causes changes in the energy band structure of atoms in the platinum monolayer compared to the energy band structure of platinum in the surface layer of a bulk particle. This is confirmed by the binding energy values of Ru@Pt and platinum nanoparticles obtained by X-ray photoelectron spectroscopy. It was shown that in this case the binding energies of adsorbates decrease.[201] In particular, calculations predicted that the surface of bimetallic particles is less saturated with carbon monoxide than the Pt(111) surface under identical conditions.[202, 203] Therefore, it is quite probable that in atmosphere with high concentration of CO the surface of Ru@Pt nanoparticle will contain much more CO-free active sites than the Pt(111) surface. Based on the available experimental data and on the results of calculations, mechanisms of the PROX reaction on bimetallic particles and on monometallic platinum were proposed. The higher selectivity of Ru@Pt nanoparticles compared to platinum in this reaction got an explanation. Low temperatures of CO and H_2 oxidation onset (20 and 25 °C, respectively) were established experimentally and substantiated within the framework of the proposed mechanism of oxygen dissociation involving hydrogen. This offers new prospects for *ab initio* design of improved catalysts of the PROX reaction and, probably, anodic catalytic coatings for low-temperature fuel cell applications with high tolerance to carbon monoxide.

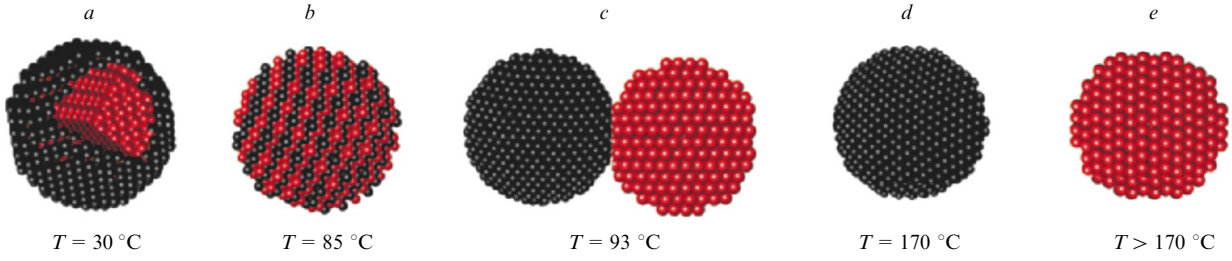


Figure 7. Schematic representation of Pt- and Ru-containing nanoparticles.[193]
Ru@Pt core–shell particle (*a*), PtRu alloy particle (*b*), mechanical mixture of Pt and Ru particles (*c*), monometallic Ru particle (*d*) and monometallic Pt particle (*e*).
Shown are the temperatures corresponding to efficient cleaning of hydrogen from CO impurity in the presence of these particles.

V. Conclusion

An analysis of the results reported in this review showed that introduction of the second metal into the monometallic catalyst to give binary alloy particles with new structural organization of the surface leads to nonadditive enhancement of catalytic properties, *i.e.*, the synergistic effect. Considerable attention to this effect is due to the need for the development of (i) the foundations of catalysis and (ii) approaches to the design of high-performance new-generation catalysts. Successful design of nanosized new-generation catalysts is favoured by progress in (a) physical methods of investigation of surfaces, suitable for identification and characterization of surface active sites on the atomic level and (b) methods for the synthesis of catalysts with control of particle size, shape and chemical composition.

Development of experimental investigations in catalysis is accompanied by rapid progress in computational methods of quantum chemistry and modelling. Modern *ab initio* calculations extend and deepen the knowledge on the structure of the surface of heterogeneous catalysts, predict the reactivity of active sites to reactants and products, disclose the role of promoters and provide better insight into reaction mechanisms. The results obtained in the original studies and cited in this review make it possible to correct our vision of the phenomenon of synergistic effect in the reactions on bimetallic alloys: structural organization of the surface of alloys under the action of the co-component *in situ* is the essence of synergism in catalytic action. There are grounds to believe that further progress in the studies on the synergistic effect in catalysis will allow one to predict the scale of the effect and to offer prospects for the design of novel industrial catalysts that should combine high activity, selectivity and stability with low content of supported noble metals.

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