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Cement-containing catalysts

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ABSTRACT. The most important achievements in the development and use of cement-containing catalysts for a number of organic and inorganic processes have been reviewed. The possibilities for development in this branch of catalysis have been discussed.

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I. Introduction

Industry is making increasing demands in relation to the activity, selectivity, operational lifetime, mechanical strength, and durability of catalysts. A new direction in the solution of these problems is being opened up by the inclusion of aluminates of calcium (AC) and cements in catalytic compositions. These catalysts are used in the transformation of hydrocarbons, the conversion of methane and naphtha, the purification of gases from oxides of carbon, the dissociation of ammonia, sulphur purification, the conversion of carbon monoxide, the production of glycerol, etc.[1–8] Various aspects of the use of cements for these purposes may be noted.

1. One of the features of cements favouring their use in catalysis is their high mechanical strength. 2. The efficiency of both low-temperature and high-temperature processes depends on the thermal stability of heterogeneous catalysts, and heat resistance is an inherent property of alumina cement.[9] 3. The stability of catalysts used in the treatment of hydrocarbon raw material is determined to a large extent by their stability to coke formation. The cost of combating coke formation sometimes exceeds the cost of the actual catalytic processes.[10] One method of eliminating or preventing coke formation is by introducing basic additives, in particular as cements. 4. The large-scale production of cements, combined with the restricted supply of raw materials for the production of carriers (Al_2O_3, MgO, SiO_2, etc.), has provided a convincing reason for using various cements, in particular high-alumina cements, for this purpose. 5. The important role of the carrier in the production of heterogeneous contact catalysts[11] makes it necessary to study the texture of calcium aluminate sorbents and to develop carriers with a highly developed and controllable surface.[12] 6. Finally, the use of cements in catalysts is encouraged by the efforts to combine a high activity of catalytic systems with ecological cleanliness and waste-free methods of production.

II. The mechanism of formation of cement-containing contact catalysts

In the late sixties and early seventies, the study of the mechanism of formation of nickel-cement (nickel–aluminium–calcium) catalysts obtained by chemical mixing,[7,8,13,14] led to the discovery of the reaction of the cements (calcium aluminates) with the source of the active component (the nickel salts) in the aqueous medium. The reaction takes place at room temperature, and is accompanied by marked changes in texture and phase composition. This made it necessary to re-examine the view that the calcium aluminates and cements were merely hydraulic binding agents.

It was subsequently shown that the mechanism of the reaction of basic metal carbonates with calcium aluminate cements is the same for nickel,[7,8,13–23] zinc,[17,19–26] copper,[17,19–23,27] cobalt,[19–23] copper–zinc,[28] cobalt–manganese,[29] and cobalt–copper[30] contact catalysts. Metal hydroxide carbonates (MHC) react with calcium aluminates in aqueous or aqueous–ammoniacal media to give a multi-phase system. The composition of the reaction products indicates both hydration of the cements and an exchange reaction between the calcium aluminates and the metal hydroxide carbonates. Depending on the conditions, the reaction gives the metal hydroxoaluminates, $CaCO_3$, $Al(OH)_3$, $M(OH)_2$, $Ca_3[Al(OH)_6]_2$, and $Ca(OH)_2$. The metal hydroxoaluminates (MHA) have the following characteristics: a, their structure contains water as OH groups; b, the ratio M/Al in them is close to 1.5, particularly in an aqueous medium, but not in an aqueous–ammoniacal medium, in which some of the metal is lost as ammines; c, they can be synthesised from salts, which act as the source of the metal and aluminium, the latter being present as the $Al(OH)_4^-$ anion; d, on thermal decomposition they give MO and MAl_2O_4, so that in the original MHA the molar ratio $MO/Al_2O_3 > 1$; e, many metal hydroxoaluminates have the formula $M_3Al_2(OH)_{12}$. Since calcium hydroxoaluminates on dissolving in water give Ca^{2+} and $Al(OH)_4^-$, the reaction of MHC with alumina cements can be represented as follows: Ca^{2+} ions react with CO_3^{2-} ions in the labile structure of the MHC to give sparingly soluble $CaCO_3$, whose formation displaces the reaction to the right. To preserve the electrical neutrality of the MHC, the place

of one CO_3^{2-} ion carrying two negative charges must be taken by two $Al(OH)_4^-$ ions, each of which carries only one negative charge:

$$a\,[m\,MCO_3 \cdot n\,M(OH)_2] + 3\,Ca^{2+} + 2\,Al(OH)_4^- + 4\,OH^- = \\ = M_3Al_2(OH)_{12} + (3 - am)\,Ca(OH)_2 + (an + am - 3)\,M(OH)_2 + \\ + am\,CaCO_3, \quad (1)$$

$m \leqslant n;\ m = 1, 2;\ n = 1, 2, 3$

Since $M_3Al_2(OH)_{12}$ has a layer crystal lattice, insertion of $M(OH)_2$ into it is possible, so that the ratio M/Al will increase. In addition to metal hydroxoaluminates, hydroxocarbonatoaluminates may also be formed:

$$a\,[m\,MCO_3 \cdot n\,M(OH)_2] + 3Ca^{2+} + 2\,Al(OH)_4^- + 4\,OH^- = \\ = M_3Al_2(OH)_8(CO_3)_2 + (5 - am)\,Ca(OH)_2 + \\ (an + am - 3)\,M(OH)_2 + (am - 2)\,CaCO_3. \quad (2)$$

The reactions of MHC with calcium mono- and dialuminates are described by the equations

$$3\,CaAl_2O_4 + 12\,H_2O + a\,[m\,MCO_3 \cdot n\,M(OH)_2] = \\ = am\,CaCO_3 + \left(\frac{3 - am}{3}\right)Ca_3[Al(OH)_6]_2 + \\ + \left(\frac{an + am}{3}\right)M_3Al_2(OH)_{12} + \left(\frac{12 - 2an}{3}\right)Al(OH)_3, \quad (3)$$

$$3\,CaAl_4O_7 + 21\,H_2O + a\,[m\,MCO_3 \cdot n\,M(OH)_2] = \\ = \left(\frac{an + am}{3}\right)M_3Al_2(OH)_{12} + am\,CaCO_3 + \\ + \left(\frac{3 - am}{3}\right)Ca_3[Al(OH)_6]_2 + \left(\frac{30 - 2an}{3}\right)Al(OH)_3 \quad (4)$$

In an aqueous–ammoniacal solution, part of the MHC is converted into a carbonatoammine complex. The composition of the reaction products and the extent of the reaction depend on the numerical values of the coefficients *a*, *m*, and *n* (if M = Ni or Co, *m* = 2 and *n* = 3; if M = Zn, *m* = 1 or 2 and *n* = 3; if M = Cu, *m* = *n* = 1). The reactions according to Eqns. (1)–(4) are determined by the ratio of *a* to the values of *m* and *n*. With increase in *a*, the yield of $CaCO_3$ and $M(OH)_2$ increases, and the proportion of $Ca(OH)_2$ decreases. At certain ratios, the reaction will take place according to different stoichiometric equations. Thus when M = Ni, Cu, Zn, or Co, $M(OH)_2$ must take part in the reaction at low values of *a*, and $Ca(OH)_2$ must take part at high values of *a*. The range of possible values of *a* in the case of the formation of hydroxocarbonatoaluminates [Eqn.(2)] is broader than for the formation of MHA. The phase composition of cement-containing catalysts is described extremely accurately by general equations based on the reaction between metal hydroxide carbonates and $CaAl_2O_4$ ($CaAl_4O_7$). The thermal decomposition of the compounds formed by the chemical reaction and containing the active component can be described by the equations

$$M_3Al_2(OH)_{12} \xrightarrow[-H_2O]{} 3MO.Al_2O_3\ \text{(solid solution)} \rightarrow 2MO + MAl_2O_4, \quad (5)$$

$$M_3Al_2(OH)_8(CO_3)_2 \xrightarrow[-H_2O,\ CO_2]{} 3MeO.Al_2O_3\ \text{(solid solution)} \\ \rightarrow 2MO + MAl_2O_4. \quad (6)$$

If two metal hydroxide carbonates take part in the reaction simultaneously (Cu and Zn, Co and Cu, Ni and Cu), the first stage of the reaction gives mixed hydroxide carbonates, from which are formed mixed hydroxoaluminates (possibly hydroxocarbonatoaluminates), which are readily converted into mixed solid solutions

$$m'M'CO_3.n'M'(OH)_2 + m''M''CO_3.n''M''(OH)_2 + CaAl_2O_4(CaAl_4O_7) \\ + H_2O \rightarrow M'M''Al_2(OH)_{12} \\ \rightarrow M'O.M''O.Al_2O_3\ \text{(solid solution)}. \quad (7)$$

Solid solutions of mixed metal hydroxoaluminates and hydroxocarbonatoaluminates are formed from the anion-modified oxides (anionic group OH^- or CO_3^{2-}),[11] that is the oxides of Al, Cu, Co, Ni, Zn; naturally, the solid solutions obtained are also anion-modified.

The reaction of metal hydroxide carbonates with Ca^{2+} and $Al(OH)_4^-$ ions, represented by Eqn. (1) above, can be represented differently:

$$m\,MCO_3 \cdot n\,M(OH)_2 + m\,Ca^{2+} + 2m\,Al(OH)_4^- \rightarrow \\ \rightarrow m\{M[Al(OH)_4]_2\} \cdot n\,M(OH)_2 + m\,CaCO_3.$$

Table 1. Composition of the MHC and MHA, the ratio MO/Al_2O_3 in the MHA, and the composition of the thermal decomposition products of the MHA.

MHC $mMCO_3.nM(OH)_2$	MHA $M_{m+n}Al_{2m}(OH)_{8m+2n}$	MO/Al_2O_3	MHA thermal decomposition products $nMO + mMAl_2O_4$, n/m
M = Ni, $m = 1$, $n = 1$	$Ni_3Al_2(OH)_{12}$	3:1	2:1
M = Co, $m = 1$, $n = 2$	$Co_3Al_2(OH)_{12}$	3:1	2:1
M = Cu, $m = 1$, $n = 1$	$Cu_2Al_2(OH)_{10}$	2:1	1:1
M = Zn, $m = 2$, $n = 3$	$Zn_5Al_4(OH)_{22}$	5:2	3:2
M = Zn, $m = 1$, $n = 3$	$Zn_4Al_2(OH)_{14}$	4:1	3:1

The hydroxoaluminates $m\{M[Al(OH)_4]_2\}.nM(OH)_2$ can be represented as $M_{m+n}Al_{2m}(OH)_{8m+2n}$. Thus depending on the composition of the MHC, the products are different MHA with different ratios MO/Al_2O_3, which determine the composition of the thermal decomposition products (see Table 1). Table 1 shows that: a, the composition of the MHA depends markedly on the composition of the MHC; b, the ratio MO/Al_2O_3 in the MHA is always greater than 1; c, the molar ratio $MO/M'Al_2O_4$ in the thermal decomposition products of the MHA, that is the ratio of the free metal oxide to the spinel, is exactly equal to n/m. If the exchange of the ions CO_3^{2-} and AlO_4^- in incomplete, its products will be hydrated metal carbonatoaluminates, and since the number of AlO_4^- ions introduced into the structure is lowered, the ratio MO/Al_2O_3 will be increased.

III. Carriers and adsorbents based on cements

A source of calcium–aluminium carriers and adsorbents is provided by calcium mono- and dialuminates $CaAl_2O_4$ (CA) and $CaAl_4O_7$ (CA_2), which are the principal phases in high-alumina cements. The first stage in the preparation of these carriers is

hydration, which at elevated temperatures gives mainly $Ca_3[Al(OH)_6]_2$ (C_3AH_6):†

$$3CaAl_2O_4\,(CA) + 12H_2O = Ca_3[Al(OH)_6]_2\,(C_3AH_6) + 4Al(OH)_3 \quad (8)$$

$$3CaAl_4O_7\,(CA_2) + 21H_2O = Ca_3[Al(OH)_6]_2\,(C_3AH_6) + 10Al(OH)_3 \quad (9)$$

At lower temperatures, the less stable products C_2AH_8 and CAH_{10} are formed. The compound C_3AH_6 [31] can be obtained either from Ca and Al hydroxides or from the metastable C_2AH_8 and C_4AH_9, which at 25 °C are readily converted into stable C_3AH_6. Amorphous $Al(OH)_3$ is the primary hydration product of calcium aluminates.[31] With the passage of time, that is on ageing, at a suitable pH, amorphous $Al(OH)_3$ crystallises, forming boehmite and hydrargillite (gibbsite).[31,32] Thermodynamic analysis of the hydration of calcium aluminates[9,31–34] confirms that reactions (8) and (9) are possible. The hydroxide $Al(OH)_3$ is formed in the hydration of C_3A, $C_{12}A_7$, CA, and CA_2, and $Ca(OH)_2$ is formed in the reaction of $C_{12}A_7$ with water. Highly basic hydrated Ca aluminates are formed by the reaction of Ca and Al ions in solution and in phase transformations of hydrated calcium aluminates involving OH^-; part of the Al passes into solution as anions. With increase in the basic character of the hydrated Ca aluminates, the probability of their formation increases. Reactions involving $Al(OH)_3$ are thermodynamically more favourable than those with aluminate anions. During hydration and on ageing, the unstable compounds are converted into more stable compounds,[9] in particular into C_3AH_6. The thermal decomposition of hydrated calcium aluminates, the hydration products of anhydrous calcium aluminates, at different temperatures gives $C_{12}A_7$, CaO, Al_2O_3, $Ca(OH)_2$, and other compounds containing Al and/or Ca.[2,7,9,12,15,16,23,32–37] A method has been developed for obtaining the carrier and adsorbent galyumin with a highly developed surface based on calcium monoaluminate (CA).[12,38] X-Ray diffraction has shown that the hydration of CA gives hydrated calcium aluminates, $Al(OH)_3$, and $CaCO_3$; the latter is produced by the reaction of CA with atmospheric CO_2 and with carbonate-containing reagents. To produce an adsorbent with the most highly developed surface, it is necessary to intensify the hydration processes throughout the entire volume of the CA, to break down the layer of $CaCO_3$ and $Al(OH)_3$, and also to extract part of the Ca. The adsorbent and catalyst (galyumin) obtained has not only a highly developed surface (the specific surface increases from 2–4 $m^2\ g^{-1}$ to 400 $m^2\ g^{-1}$, that is by two powers of ten), but also a high mechanical strength.

The aluminium–calcium components of the catalysts have been studied.[39] In one series of experiments, the hydration of CA according to Eqn. (8) was carried out, and the $Al(OH)_3$ formed was combined with the calculated quantity of $Ca(OH)_2$ to give C_3AH_6. In another series of experiments, C_3AH_6 was synthesised by the direct reaction of $Al(OH)_3$ with $Ca(OH)_2$. Thermal decomposition of C_3AH_6 gave the product $12CaO.7Al_2O_3$, that is $Ca_{12}Al_{14}O_{33}$, or $C_{12}A_7$. Some authors[40–42] suggest that water in quantities not less than 1.4% is retained in the $C_{12}A_7$ structure up to high temperatures (1000–1100 °C), and that $C_{12}A_7$ in fact has the composition $12CaO.7Al_2O_3.H_2O$. The properties of $C_{12}A_7$ are such that this water is assumed to be "zeolitic". According to Mamaeva and co-workers,[39] the phase $C_{12}A_7$ is produced at 400 °C; its concentration increases continuously with increase in the heating temperature to 1000 °C. This phase has a highly developed surface, which is preserved even at 800–1000 °C. The higher the degree of dispersion of the phase C_3AH_6 in the unheated specimens, the higher the specific surface (S_{sp}) of the product $C_{12}A_7$ after heating. The data obtained[39,43] have been used to develop a method for obtaining an aluminium–calcium carrier and adsorbent (galyumin-Ts) with a thermally stable texture (withstanding thermal treatment at 600–1000 °C) and a mechanical strength up to 500–700 kg cm^{-2}.

A study of the infrared spectra[44,45] of a number of calcium aluminates (CA, CA_2, $C_{12}A_7$) and catalysts and adsorbents based on them, with different S_{sp} (30–400 $m^2\ g^{-1}$), showed that the bands in the range 400–900 cm^{-1} are due to the vibrations of aluminium–oxygen tetrahedra in the framework zeolite-like structure. The calcium ion apparently acts as compensating cation. Depending on the method of preparation, the value of S_{sp}, and the concentration of CaO, the aluminium–calcium adsorbents and catalysts can be divided into two groups: a, those with a framework structure containing calcium aluminates; and b, those consisting chiefly of γ-Al_2O_3 modified by calcium. The water in the aluminium–calcium adsorbents and catalysts is present in different states; it may be adsorbed, form surface OH groups, and be present as $Ca(OH)_2$, $Al(OH)_3$, and hydrated calcium aluminates. From an analysis of infrared data on the hydration of the calcium aluminates CA, CA_2, C_3A, and $C_{12}A_7$,[9,46] it was suggested that the high strength of cement block is achieved as a result of the formation of Al–O–Al structural bonds between the octahedra of aluminium hydroxide and hydrated calcium aluminates. The highly developed thermally stable porous structure of an adsorbent based on calcium aluminates (novogal), and the possibility of controlling this structure, open up the possibility of using novogal for the gas-chromatographic separation of complex mixtures of C_1–C_4 hydrocarbons.[47,48] From the nature of its reaction with an adsorbate, novogal must be classified as a specific adsorbent of type II.[49]

The genesis of the phase composition and texture of a carrier, adsorbent, and catalyst based on calcium–aluminium cement (talyum), whose mineralogical components are CA and CA_2, have been studied.[50] When talyum is treated with water under the conditions of the preparation of cement-containing catalysts, the original phases (CA, CA_2) dissolve in the first stage (the mixing stage), after which the nuclei of metastable (C_2AH_8, C_4AH_{13}) and stable (C_3AH_6, gibbsite) hydrated new formations separate from the supersaturated solution. The fact that the hydration product of Al_2O_3 is produced in the hydration of aluminium–calcium cements and subsequent thermal decomposition provided the starting point for the production and study of two-component γ-Al_2O_3–CA and γ-Al_2O_3–CA_2 compositions.[51,52] Their mechanical strength reaches 1450 kg cm^{-2} and 1000 kg cm^{-2} for the compositions 40% CA–Al_2O_3 and 20% CA–Al_2O_3 respectively. The highest mechanical strength corresponds to the texture in which a maximum contribution to S_{sp} is made by the narrow pores, and a minimum contribution by the wide pores.

The processes taking place in the production of catalysts based on calcium aluminates have been studied by high-resolution ^{27}Al NMR.[53] The structure of anhydrous calcium aluminates (CA, CA_2, C_3A, $C_{12}A_7$, talyum) contain aluminium–oxygen tetrahedra; the aluminium atoms in the tetrahedra are of different types, and their non-equivalence increases on going from highly basic to weakly

† The following notation is used in the chemistry of cements: C = CaO, A = Al_2O_3, H = H_2O.

basic aluminates. On hydration, which is one of the stages of the production of aluminium–calcium catalysts and carriers, the process $[AlO_4] \rightarrow [AlO_6]$ takes place, and the process $[AlO_6] \rightarrow [AlO_4]$ takes place on thermal decomposition. The non-equivalence of the aluminium atoms in tetrahedral coordination decreases, and the ratio $[AlO_4]/[AlO_6]$ decreases with increase in the degree of hydration. The presence of a framework of aluminium–oxygen $[AlO_4]$ tetrahedra in anhydrous calcium aluminates makes their structure similar to that of zeolites.[44,45] For zeolites, Loewenstein's rule applies; according to this rule, two aluminium atoms in tetrahedral coordination should not have a shared oxygen atom. The structure of calcium aluminates clearly indicates that Loewenstein's rule is not universal.[54] A quantum-chemical analysis of this rule for aluminium-containing catalysts and adsorbents[55] showed that a structure in which two $[AlO_4]$ tetrahedra have a shared oxygen atom is stabilised by a metal ion acting as compensating cation. The reactivity of calcium aluminates with respect to water, which is of considerable importance in the production of aluminium–calcium catalysts, also depends on distortions in the oxygen environment of calcium, and in particular on the Ca–O distances; the shorter this distance, the higher the reactivity of the calcium aluminate with respect to water.[53] Thus the rate of hydration decreases in the order $C_3A < C_{12}A_7 < CA < CA_2$,[56] and the shortest Ca–O distance increases in the same order from 2.26 Å to 2.33 Å.

Thermal desorption, thermal analysis, and X-ray diffraction have been used to study the reaction of water vapour with the aluminium–calcium components of catalysts based on calcium aluminates.[57] The presence of $C_{12}A_7$ is responsible for the increased adsorption of water vapour and the specific form of the thermal-desorption spectrum. The reaction of water vapour with the aluminium–calcium components of the catalysts, unlike the liquid-phase reaction, is not accompanied by a change in the phase composition, and this makes possible the extensive use of these catalysts in gas-phase processes involving water. Millimetre-wave spectroscopy has shown[58] that in the liquid phase, the quantity of immobilised water in $C_{12}A_7$ is more than 100 times the capacity of a monolayer, and this has been attributed to the filling of the cavities in the structure and the superposition of the chemical reaction of $C_{12}A_7$ with water on the adsorption process. The increase in the rate of hydration of aluminate cement[32] with increase in its degree of dispersion is due both to an increase in the surface area and to activation of the reacting particles. The last factor may predominate, as observed in the mechanical activation of calcium aluminates by treatment in mills without change in the degree of dispersion.[59]

Infrared spectroscopy in diffuse scattered light has been used to study the hydroxyl covering and adsorption centres of aluminium–calcium catalysts and carriers with a highly developed surface.[60] The presence of surface OH groups of several types was established. A quantitative infrared spectroscopic study of the basic and acidic (aprotic) centres from the adsorption of deuteriochloroform and CO respectively[61,62] revealed the existence on the surface of two types of aprotic acidic centre, one of which was combined with Ca ions (type I), and the other with Al ions (type II). With increase in the degree of hydration of the calcium aluminates, the concentration of the centres of type I decreases more extensively than that of the centres of type II, corresponding to the greater degree of displacement of calcium ions from the lattice, compared with aluminium ions. Three types of basic centre were detected: the strength of the centres of one type is similar to that of the basic centres in γ-Al_2O_3; other stronger centres correspond to the oxygen in the Al–O–Ca structure; and, finally, the third and strongest centres correspond to the oxygen in the Ca–O structure. According to Sominskii and co-workers,[17,52,63–65] calcium aluminates with a highly developed surface (galyumins) also show Brönsted acidity, detected using butylamine and pyridine; the adsorption of pyridine and acetone also detected Lewis centres, and the adsorption of hexadeuterioacetone detected basic centres. A thermally stable catalyst carrier[66] and an adsorbent[67] are obtained from Al hydroxides and Ca oxide, hydroxide, and carbonate. A carrier based on calcium aluminates has a high S_{sp} and is suitable for use over a wide temperature range, 400–900 °C.[68] Calcium aluminates with a highly developed surface and a high reactivity can be obtained directly from molten Al and Ca nitrates,[69] that is by simple mixing using effluent-free technology.[38,39,43,48,50,51] Thermal-desorption studies of the adsorption of CO_2, H_2O, O_2, and H_2 on calcium aluminates with different CaO/Al_2O_3 ratios and different phase compositions (CaO, C_3A, $C_{12}A_7$, CA, CA_2) [70] indicate that the adsorption bonds are extremely strong. Thus H_2O is desorbed at 930 °C ($C_{12}A_7 . H_2O$), O_2 at 720–825 °C, and CO at 450 °C and 600–760 °C.

Ca, Sr, and Ba aluminates have much in common; they all have high melting points and similar densities, mechanical strength, and tendency to undergo hydration. They are therefore all used in the same way in the production of ceramics, binding agents, and sintering cements.[35] A significant feature is that the crystal structures of the alkaline earth metal monoaluminates are based on $[AlO_4]$ tetrahedra sharing oxygen atoms.[35,71,72] The aluminate $SrO.2Al_2O_3$ is a structural analogue of $CaO.2Al_2O_3$,[35,73] and $3CaO.Al_2O_3$, $3SrO.Al_2O_3$, and $3BaO.Al_2O_3$ are also isostructural.[35] Carriers and adsorbents based on Ca, Sr, and Ba aluminates should therefore show similar behaviour. Thus the addition of Ca, Sr, and Ba oxides to γ-Al_2O_3 decreases sintering and leads to the preservation of a comparatively highly developed surface on formation of the corresponding aluminate.[74–76] The great importance of zeolites in catalysis is drawing attention to cement–zeolite compositions.[77–79] Binders with different compositions based on Portland cement gain strength rapidly, have a high resistance to wear, and can be used to encapsulate sorbents and catalysts.[80] A composition using natural zeolites appears promising.[81–83] Mixed cements containing zeolite have a high strength.[81,82] The use of Portland cement as binding agent makes it possible to obtain granulated NaA zeolites with a high mechanical strength, minimum secondary porosity, and high adsorbing power.[84]

IV. The production of metal-cement catalysts

The formation processes have been studied most intensively for nickel-cement catalysts, which are widely used in the hydrogenation of oxides of carbon, the decomposition of ammonia, the conversion of methane, the hydrogenolysis of glucose, etc.[1,2,3,6,85–87] Thus the synthesis of ammonia in plants with high unit output involves the production of synthesis gas by the conversion of methane and purification on nickel contact catalysts. The production of ammonia and hydrogen alone uses up about 30% of the total world production of catalysts. Cements are used to obtain nickel-cement contact catalysts in three ways: a, calcium aluminates are used as one of the chemical reagents reacting with the source of the active component; b, calcium aluminates are added to the catalyst mass as a binding agent to produce a strong hardened structure by moist-air treatment (MAT) or hydrothermal treatment (HTT); and c, to

combine the processes of contact catalyst formation and hydration hardening of the calcium aluminates, the original components are mixed to give a uniform mixture (alternatively, the mixing is carried out at low liquid : solid ratios), which in the form of tablets are subjected to HTT.[19,20,22,23,88–90] The reactions described by Eqns. (1)–(4) take place in the liquid medium.[7,14,89–91] In the presence of Ni salts, the phases C_2AH_8 and CAH_{10} are not detected. With increase in the ratio Ni salt/cement (CA, CA_2 talyum), the quantity of $CaCO_3$ formed increases, $Ca(OH)_2$ disappears, and $Ni(OH)_2$ appears. In complete accordance with Eqn. (3), with increase in the concentration of nickel hydroxide carbonate, the quantity of $CaCO_3$ (criterion of the exchange reaction) and S_{sp} (criterion of the development of the surface) pass through a maximum.[8] The CO_3^{2-} ion evidently does not enter the structure of the hydrated aluminate, since if a compound of the type $M_3[Al(OH)_4(CO_3)]_2$ were formed, the $CaCO_3$ concentration would have decreased and would differ significantly from that calculated from Eqn. (3). The reactions between calcium aluminates and Ni hydroxide carbonate can take place by a liquid-phase or a solid-phase mechanism, depending on the composition of the medium (water, aqueous ammonia solution) and the liquid : solid ratio. The Ni hydroxoaluminate formed in reactions (3) and (4) decomposes when heated according to Eqn. (5) to give a poorly crystalline disordered $NiO-Al_2O_3$ solid solution, whose structure is perfected at 400–1000 °C, accompanied by the gradual liberation of the excess NiO.[90] Ni hydroxoaluminate is the main form in which the active component exists in the catalysts at the stage preceding thermal decomposition and activation. Since the reaction of the components is limited by the rate of solution of the calcium aluminates (talyum) in aqueous ammonia solution, an effective method of increasing the extent of the reaction is by increasing the degree of dispersion and the ratio CA/CA_2.[92] On thermal treatment, the phase CaO formed by the high-temperature decomposition of $CaCO_3$ reacts with Al_2O_3, preventing the reaction of the superstoichiometric NiO with Al_2O_3 and decreasing the rate of formation of spinel ($NiAl_2O_4$).[92] The specific surface of the nickel catalysts is determined by the value of S_{sp} of the dispersed phase of the $NiO-Al_2O_3$ solid solution. High-temperature X-ray diffraction has shown that nickel–aluminium–calcium catalysts are reduced in two stages, at 400–600 °C and 600–800 °C. The presence of compounds difficult to reduce ensures the preservation of a high degree of dispersion of metallic nickel over a wide temperature range and creates conditions for the effective use of aluminium–calcium-based catalysts in high-temperature processes (conversion of hydrocarbons, decomposition of NH_3). A composition containing CA, CA_2, and Al_2O_3 together with nickel can be used to produce an optimum catalyst for low- and high-temperature processes.[89–91] According to Dzis'ko,[4] mixing does not make it possible to achieve the same extent of reaction between the components as the combined precipitation of $Ni(OH)_2$ and $Al(OH)_3$ and the coprecipitation of $Ni(OH)_2$ on an Al_2O_3 carrier. The nickel–aluminium–calcium system (and, as shown below, all other systems based on calcium aluminates) is an exception to this rule. In this case the product is formed by a new mechanism, in which the original components, on chemical mixing, react with one another practically completely under very mild conditions:

$$\begin{array}{c} Ni_3CO_3(OH)_4\cdot 4H_2O + CaAl_2O_4 + CaAl_4O_7 \rightarrow \\ \rightarrow Ni_3Al_2(OH)_{12} + CaCO_3 + Al(OH)_3 \\ \downarrow 350^\circ C \qquad\qquad \downarrow 740^\circ C \qquad \downarrow 300^\circ C \\ (NiO)_3{-}Al_2O_3 \qquad\quad CaO \qquad Al_2O_3 \\ \downarrow 400\text{–}1000^\circ C \qquad\quad \downarrow 800\text{–}1000^\circ C \\ x\cdot NiO + (NiO)_{3-x}\cdot Al_2O_3 \qquad\quad CaAl_2O_4 \end{array} \qquad (10)$$

X-ray diffraction, texture, thermochromatographic, and spectral studies[90,93–99] confirm that a multiphase system with a highly developed surface is formed. Change in the ratio of Al_2O_3, CA, and CA_2 [89,90] makes it possible to control the degree of dispersion, phase composition, and mechanical strength of Ni catalysts. The plastic deformation of $CaCO_3$ on pressing leads to an increase in the unit contact strength; the mechanical strength increases with increase in the $CaCO_3$ concentration. The sharp increase in strength at high pressing pressures (800–1000 MPa)[100] indicates plastic deformation of the structure-forming particles, in particular calcite. The increased strength of the bond between NiO and the carrier is confirmed by the thermal-vacuum electrical conductivity curves.[101]

V. Catalysts for the methanation of oxides of carbon

In the catalytic purification of technical gases (nitrogen–hydrogen mixture, hydrogen, etc.) from CO and CO_2, the concentration of oxides of carbon at the outlet should not exceed 10–20 $cm^3\ m^{-3}$ (10–20 p.p.m.). The catalytic purification from CO and CO_2 is based mainly on their exothermic hydrogenation to CH_4 (so-called methanation). Methanation can be carried out for different purposes: to remove poisons (CO, CO_2), to obtain a fuel gas, and to transfer the heat of hydrogenation to a distance.[1,102,103] The most suitable catalysts for purifying hydrogen-containing gases from CO and CO_2 are nickel catalysts; they are more active and more selective than iron catalysts, and less expensive than contact catalysts based on the Pt group metals.[85,86,102] Catalysts for purification from CO and CO_2 must satisfy severe requirements in relation to: a, activity; b, thermal stability (the activity should be preserved on superheating, which usually takes place with an increased concentration of CO_2 and CO at the inlet); c, stability, that is resistance to the action of the reaction medium; and d, mechanical strength. Mechanical strength is particularly important when large quantities of catalyst, up to 50 tons, are loaded into the methanation vessels in plants with a high unit output (in particular in NH_3 synthesis plants with an output of up to 1360 tons per day). These requirements are satisfied by Ni contact catalysts based on cement (aluminium–calcium).[7,14,89–91,102,104–115] By selecting the reaction medium, it is possible to control the ratio between the oxide and metallic phases.[93,97] An important part in the production of the contact catalysts is played by the change in the oxygen coordination of aluminium from tetrahedral (Al_t) to octahedral (Al_o) on hydration and from Al_o to Al_t on thermal treatment.[16,98]

The reduction of nickel–aluminium–calcium contact catalysts to give a metallic nickel phase involves several stages. The low-temperature stage (160–400°) involves the reduction of free nickel oxide, and the high-temperature stage involves the reduction of

combined oxide. The second stage may be necessary for the following reasons: a, the difficulty of reducing nickel in CaO–NiO solid solutions; b, the formation of nickel aluminium spinel; and c, the replacement of the metal ion in the zeolite-like structure of the aluminates. The principal form of existence of the precursor of the active form of nickel is nickel hydroxoaluminate, which on thermal decomposition is converted into $NiO-Al_2O_3$ solid solutions.[90] There is restricted mutual solubility of the components, however, in the NiO–Ca(Ba)O system.[116–118] Extensive reaction of nickel oxide with calcium aluminates does not give contact catalysts with a high activity in low-temperature hydrogenation processes. To avoid this limitation, Al_2O_3 is added to the catalyst together with calcium aluminates.[119] The NKM-4 (4A) catalysts obtained in this way can operate at temperatures much lower than the minimum working temperatures (260 °C) for the hydrogenation of CO and CO_2, used in the large-scale production of ammonia.[8,9,108,119] Electron microscopy has shown the decisive part played by the carrier in the distribution of the particles of reduced Ni at temperatures in the range 400–800 °C.[120] Simplex lattices have been used to construct composition–property (total specific surface, surface area of the active component, S_{Ni}, mechanical strength) diagrams to find the optimum ratio of the components NiO, Ca, CA_2, and Al_2O_3.[121] It was found that the NiO–talyum reaction has a greater influence on S_{sp} than the $NiO-Al_2O_3$ reaction; the value of S_{Ni}, on the other hand, depends to a greater extent on the distribution of nickel in Al_2O_3. The change in the strength of the catalyst during hydrothermal treatment is due to the characteristics of the hardening of the binding component (cement); hydration is accompanied by the appearance of micro-strains produced by the crowded growth of the crystals of the new formations.[122] The increase in strength when the contact catalyst is heated to 400° is due to the relaxation of the strains produced on hydrothermal treatment.[123,124] The low-temperature decomposition of $CaCO_3$ has been detected in nickel-cement catalysts in which calcite appears during preparation, at temperatures $\leqslant$400 °C in reducing media.[125,126]

The purification of technical gases from CO and CO_2 on Ni contact catalysts has been studied by Kreindel' and co-workers.[127–129] In the kinetic range, the specific catalytic activity (calculated for 1 m^2 Ni) is constant and independent of the nature of the carrier, the method of preparation, and the temperatures of thermal treatment and reduction of the catalysts. With increase in temperature, the reaction passes into the outer-diffusion range.

The kinetics of the methanation of CO and CO_2 and their mixtures on the industrial nickel–aluminium–calcium catalyst[108] have been studied.[130–138] The principal kinetic characteristics of the methanation of CO are the same at atmospheric pressure and at an increased pressure (up to 3 MPa). In the combined methanation of CO and CO_2, the components have a simple influence on one another, with adsorption competition on the surface. Mass spectrometry, thermal desorption, infrared spectroscopy, and isotope studies[134–136] showed that the mechanism of the methanation does not involve the dissociative adsorption of CO and CO_2; the reaction takes place with the formation of compounds $C_xH_yO_z$ involving atomic adsorbed hydrogen. The data obtained[130–136] made it possible to put forward a new stepwise scheme for the hydrogenation of CO and CO_2, according to which both processes take place without the preliminary dissociation of CO and CO_2. In the methanation of carbon monoxide, the surface is covered by CO, and also HCO, HCOH, CH, and OH; the limiting stage is the reaction of $CH_{(ads)}$ with $H_{(ads)}$. In the methanation of CO_2; the slow stage is the reaction of $CO_{2(ads)}$ and $H_{(ads)}$, and intermediate compounds $C_xH_yO_z$ are present on the surface. These results show good agreement with published conclusions.[103,137,138] The nickel-cement catalysts NKM-4A and GIAP-16 are highly active in the methanation of stoichiometric mixtures of CO and CO_2 with H_2 in the temperature range 300–700 °C;[139] this is of undoubted interest for solving the problem of the transfer of energy over large distances by a combination of exothermic and endothermic reactions (an "Adam and Eve" process).[11]

VI. Catalysts for the conversion of hydrocarbons

One of the indicators of technical progress in developed countries is the level of output in the production of hydrogen. In recent decades, the world production of hydrogen has increased several-fold. This is due to the increase in the production of ammonia, methanol, and the products of petrochemical synthesis, and the vast contribution made to these processes by reactions involving hydrogen. One of the most widely encountered methods for obtaining hydrogen-containing gases is by the catalytic conversion of hydrocarbons.[86,140–142] The steam conversion of methane takes place at high temperatures (800–900 °C), and this naturally makes increased demands on the catalysts and makes it necessary to avoid carriers based on SiO_2, which can be carried away by the steam and deposited on the cold parts of the equipment. As a result, extensive use has been made of nickel catalysts on alumina cements, calcium aluminates, and Al_2O_3 containing alkaline earth metal oxides as promoters.[87,140,141] High-temperature treatment of the carrier or catalyst mass leads to the formation of Ca, Sr, and Ba aluminates in the surface layers or throughout the entire volume of the contact catalyst. To avoid coke formation on catalysts in the conversion of hydrocarbons, attempts were made to introduce a hydraulic cement as early as the nineteen-thirties.[143] The introduction of cements into a mixture of nickel salts and activators gave catalysts with a successful combination of high mechanical strength, stable activity, and resistance to coke formation.[144] A cement-containing nickel catalyst with a high mechanical strength (400 kg cm^{-2}) has been described.[145] The most active catalysts for reforming CH_4 with steam or a mixture of steam and O_2 are contact catalysts including Al_2O_3, CaO, and NiO.[146,147] A catalyst based on alumina with added Ca and Mg oxides has an increased thermal stability and mechanical strength.[147] An Ni/Al_2O_3 catalyst promoted by CaO is used for the steam conversion of petroleum.[148] Nickel-containing contact catalysts produced in the USSR are being used successfully: GIAP-16 (24–26% NiO, 55–59% Al_2O_3, 14–16% CaO, 0.8–1.2% BaO) and KSN-2 (12–15% NiO, 80–83% Al_2O_3, 3% CaO, 1% MgO).[85,149] The use of nickel on a cement carrier makes it possible to carry out the steam reforming of C_2 and higher hydrocarbons with a low steam consumption without coke formation.[150] A mechanically strong catalyst with a long working life and high activity in the steam reforming of hydrocarbons contains a mixture of calcium aluminates and nickel, promoted by a Ba salt.[151] The nickel catalysts based on calcium aluminates C11-2, C11-5, and C11-25 [152] were developed for the steam conversion of petroleum fractions, where there is a danger of extensive coke formation on the contact catalysts and it is necessary to use high steam/hydrocarbon ratios. A stable catalyst for the reforming of hydrocarbons with steam, resistant to coke formation, contains an aluminate cement and a mixture of Ni and Mg oxides.[153] The activity and specific surface of nickel–aluminium–calcium catalysts increase with increased concentrations of Al_2O_3 and

CaO.[154] The effective high-temperature catalyst GIAP-16N for the conversion of CH_4 with steam is obtained by introducing CA, CA_2, and high-alumina cements into a spent nickel–aluminium hydrogenation catalyst.[155] The presence of free CaO in a composition containing NiO and an aluminate cement[156–160] apparently makes it possible, by hydration at 5–35 °C and thermal treatment at 550–1200 °C, to bind free Al_2O_3 and thus to avoid the formation of nickel aluminium spinel, difficult to reduce. The GS-12 catalyst for the conversion of methane[161] is obtained by depositing nickel on Al, Ba, and Ca oxides sintered at 1300 °C, when aluminates are formed. This catalyst can operate at high natural-gas loads and lowered steam/gas and O_2/CH_4 ratios. The residual concentration of CH_4 in the gas is 0.2–0.4%. The cement-containing catalysts for the conversion of methane, GIAP-16 and GIAP-16-2, produced in the Soviet Union, are widely used in large-scale plants for ammonia production; many of the characteristics of GIAP-16-2 match those of the CCI contact catalyst C-11-4.[162–164]

Alumina cements are often used as binding agents.[165,166] X-Ray diffraction has detected the presence of CA_6 in the nickel catalyst KSK-2 on a carrier modified by CaO or MgO.[167,168] A mixed nickel catalyst containing alumina and a fused alumina cement[169] is used to obtain H_2 from hydrocarbons with boiling points below 150 °C. Natural gas is purified from methane homologues by steam conversion at 300–400 °C in the presence of a nickel–chromium catalyst promoted by CaO and Al_2O_3.[170] An extremely productive idea has been put forward for creating a flexible technology for the production of nickel cement-containing contact catalysts for low-temperature (methanation) and high-temperature (methane conversion) processes.[1,114] An equally promising suggestion is that spent methanation catalysts be used as raw material for the preparation of GIAP-16 cement-containing contact catalysts for the conversion of CH_4.[155,171] Catalysts for the conversion of heavy petroleum residues, where the principal components of the catalysts are the calcium aluminates $C_{12}A_7$ and C_3A, have been developed.[172] The development of chemothermal methods for transferring energy over long distances using a cycle involving the steam conversion of methane and the hydrogenation of oxides of carbon required the development of thermally stable contact catalysts containing calcium aluminates.[173–175] Thermally stable and mechanically strong Cu–Ni,[176] V,[177] Rh,[178,179] Fe,[180] and Co–Mn [181,182] catalysts on an aluminium–calcium base for the conversion of hydrocarbons are also known. The base is provided by $C_{12}A_7$, CA_6, CA, CA_2,[177] and C_3A.[181] Ba aluminates, like Ca aluminates, are used successfully to produce Ni conversion catalysts.[183–185] The thermal stability of γ-Al_2O_3 is increased when its surface is modified by CaO, SrO, and BaO,[186] apparently as a result of the formation of surface layers of aluminates. With increase in the concentration of the alkaline earth metal oxides in Al_2O_3, the number of electron-donor centres increases, and this was assumed[187,188] to be related to the increase in the rate of the transformation of CH_4 in the presence of water vapour on promoted Ni catalysts. The presence of a large quantity of basic and reducing centres on the surface of aluminium–calcium carriers or Al_2O_3 modified by CaO leads to the suppression of coke formation on Ni catalysts for the conversion of hydrocarbons.[189] CaO–NiO specimens obtained by the thermal treatment of the $Ca(OH)_2$–$Ni(OH)_2$ system have a micro-structure differing markedly from that of their mechanical mixture; this is attributed to the hindered crystallisation of the oxides in the presence of one another.[189] CaO–NiO, CaO–Al_2O_3, and NiO–Al_2O_3 reactions apparently take place in nickel–aluminium–calcium conversion catalysts. In the NiO–Al_2O_3 system, even after high-temperature treatment (600–900 °C), three oxide phases are preserved: $NiAl_2O_4$ and two nickel oxides, one of which, which has a disordered crystal lattice, contains an appreciable quantity of Al ions;[190] these ions, after reduction of the catalyst, facilitate the formation of Ni crystallites with an extremely high thermal stability. Magnetic studies[191] of Ca^{2+}-promoted nickel–aluminium contact catalysts for the steam reforming of petroleum established that the reaction of metallic Ni with C_3A_5 prevents the migration of Ni over the surface and the formation of large crystallites. The high-temperature forms of adsorbed water (in $C_{12}A_7$) and oxygen may play an important role in hydrocarbon reforming processes.[70] The best carriers are calcium–aluminium cements, treated with the reaction mixture under reforming conditions and containing the phases $C_{12}A_7$ and CA.[192] When evaluating the role of individual components, it is necessary to take into account the fact that the MO–Al_2O_3 compositions (M = Ca, Sr, Ba) catalyse the reaction of hydrocarbons with steam, leading to the formation of CO and CO_2, and at the same time suppress the formation of carbon deposits.[193]

The physicochemical principles of the production and action of nickel–aluminium–calcium catalysts for the conversion of CH_4, examined briefly above, are described more fully elsewhere.[90,91,93–99,122,123] The stability and texture of catalysts are related to their phase composition.[91] It is possible to lower the Ni concentration while preserving the high activity of the contact catalyst as a result of the highly developed surface and the lowered tendency to form spinel.[194] The presence of NiO in the combined state is a condition for obtaining a thermally stable and active catalyst.[114,195] The degree of dispersion and stability of the active phase (Ni phase) depend markedly on the composition and structure of the calcium aluminate cement support.[196] Impregnating a γ-Al_2O_3 carrier with Al and Ca salts to give different calcium aluminates leads to development of the surface, stabilisation of the degree of dispersion, and increase in the stability and resistance of the catalyst to coke formation.[197]

VII. Catalysts for obtaining protective atmospheres

Controlled (protective) atmospheres and reducing media, obtained by the dissociation (cracking) of ammonia and not containing CO and hydrocarbons, are widely used in metallurgy, mechanical engineering, chemistry, and other branches of the national economy.[198–200] Protective inert atmospheres are used to prevent the oxidation and change in the chemical composition of the surface of a metal, in hot zinc plating, electrochemical tin plating, the deposition of coatings, the production of glass, and the treatment of gold and other metal articles. Throughout the world, the dissociation of ammonia is carried out in the presence of iron- and nickel-containing contact catalysts.[198–201] Catalysts for the dissociation of ammonia have to satisfy severe requirements: working temperatures 600–950 °C, concentration of residual $NH_3 \leqslant 0.05$–0.1% at volume velocities of 500–2000 h^{-1}. KDA-5 and KDA-10A nickel catalysts for the dissociation of NH_3 contain cements as components.[108,202] KDA-5 [202] is obtained by mixing nickel hydroxide carbonate (NHC) (20–50% NiO) with calcium aluminates and 25% aqueous ammonia solution. At 800 °C the residual concentration of ammonia decomposing on this catalyst (at a volume velocity of 1000–2000 h^{-1}) does not exceed 0.02–0.025% (equilibrium value 0.013%). In the production of the KDA-10 A catalyst,[108] cements are used together with Al_2O_3, making it possible to combine high activity of the contact catalyst with mechanical

strength and thermal stability. Calcium aluminates have been used as hydraulic binding agents in the production of the nickel contact catalysts KDA-3,[203] KDA-4,[204] and KDA-7.[205] The use of a combination of the properties of calcium aluminates, as components of catalytic compositions and as hydraulic binding agents, forms the basis of the nickel dissociation catalyst NKM-2A.[90,91,114] NHC, calcium aluminates, and aqueous ammonia solution are mixed at the lowest possible liquid : solid ratio (0.2–0.3). At the mixing stage, the reactivity of the cements ensures their reaction with NHC. The use of a low liquid : solid ratio made it possible to preserve most of the catalyst mass in the non-hydrated form, and to make use of the binding properties of the cements at the stage of hydrothermal synthesis and HTT. The high degree of binding of nickel in the NKM-2 catalyst ensures a lowered concentration of NiO, and the nickel phase is stable both to sintering and to binding in nickel aluminium spinel. Experience in the production and use of controlled atmospheres in ferrous metallurgy indicates the promising possibilities provided by iron-containing contact catalysts. A thermally stable catalyst should contain a refractory component, for example cements ($CaAl_2O_4$ melts at 1600 °C, and $CaAl_4O_7$ at 1750 °C). Calcium aluminates can be added either directly or as components which act as sources of Ca and Al. In the production of Fe contact catalysts by fusion, temperatures of 1500–1700 °C are sufficient for the formation of the compounds $Ca_xAl_yO_z$. Fe-containing KDA-1A,[206] KDA-2,[207] and KDA-1M[208] catalysts for the dissociation of NH_3 are obtained in this way. These catalysts contain a solid solution based on magnetite, formed with the participation of $CaAl_2O_4$. This series of catalysts with a high iron concentration (up to 77%) and a high thermal conductivity ensures the decomposition of NH_3 to a residual concentration $\leqslant 0.05-0.1\%$ at 650–950 °C. Experience in the industrial use of KDA catalysts has shown that they are capable of stable operation at temperatures of 700–900 °C and volume velocities of 1000–6000 h^{-1} for not less than 5–7 years, and can withstand brief superheating to 1000–1100 °C.[209] An important and promising development involves the dissociation of NH_3 on metal-cement contact catalysts to give a nitrogen–hydrogen mixture for the reduction of catalysts in the starting-up of assemblies when there are no other sources of hydrogen.[1,209]

VIII. Catalysts for purifying sulphur-containing gases

Sulphur compounds present in technical gases are powerful catalyst poisons, and lead to the corrosion of apparatus and contamination of the atmosphere. Industrial methods for purifying gases from harmful impurities, including sulphur compounds, can be divided into three groups: adsorption, liquid (or absorption), and chemisorption (or chemisorption–catalytic).[85] Zinc oxide absorbers remove H_2S, C_2H_5SH, and COS effectively, and CS_2 less effectively. The absorption of H_2S gives ZnS, which is stable in the reaction medium, so that this reaction is displaced completely to the right. In the production of zinc–aluminium–calcium catalysts, reactions (3) and (4) take place between $CaAl_2O_4$ ($CaAl_4O_7$) and zinc hydroxide carbonate (ZHC) to give zinc hydroxoaluminate (ZHA) and $CaCO_3$.[24,25,52,65] The thermal decomposition of ZHA is described by Eqn. (5). The source of ZnO is ZHA, where the ratio $ZnO/Al_2O_3 > 1$, and also ZHC. The morphology of zinc-cement contact catalysts[28] is characterised by the presence of different structures — block (carrier) and globular (zinc-containing component). The texture of $ZnO-CaAl_2O_4$ and $ZnO-CaAl_4O_7$ catalysts[210] is determined to a large extent by the reaction of the components. The study of the production of zinc oxide absorbers for sulphur-containing gases on $CaAl_2O_4$, $CaAl_4O_7$, and Al_2O_3 carriers[26,52,211] revealed a regular feature: the binding of ZHC in ZHA lowers the activity of the chemisorbing materials to a greater extent, the more extensive the reaction between ZHC and the carrier. The degree of binding of the zinc component in ZHA [26,101,211] decreases in the order $CaAl_2O_4 > CaAl_4O_7 > Al_2O_3 >$ galyumin, whereas the activity increases in this order.[26] Other conditions being equal, the extent of the absorption of H_2S is determined only by the concentration of the free ZnO phase. Zn^{2+} ions in tetrahedral surface centres and bulk zinc aluminium spinel are extremely stable, and this explains the inactivity of the absorbers towards H_2S and the inhibition of sulphidation processes on these contact catalysts.[212] The reaction of C_2H_5SH with absorbers based on ZnO [213] takes place in two stages: ZnS and hydrocarbon are formed initially in the sulphurisation stage, after which degradation hydrogenation, and the synthesis of sulphur-containing compounds take place on ZnS. A thermodynamic analysis[214] has shown that the presence of hydrogen in the reaction mixture prevents the decomposition of the sulphur-containing substances to sulphur, decreases the rate of formation of thiophen and thiophan, and increases the degree of purification to 80–100%. Cement provides an extremely effective means of granulating ZnO.[211,215,216] Calcium aluminates (and also Sr and Ba aluminates) have been used to develop effective zinc-containing contact catalysts for purification from sulphur.[217–219] The catalyst TsKA-1 [217] has a mechanical strength up to 350–500 kg cm^{-2} with a sulphur capacity (400 °C) of 27–33 mass%. The presence of CaO in the cements increases the absorbing power.[220,221] Special-purpose zinc-containing cements are of interest for catalysis.[222–224] One promising method for purifying industrial effluent gases with the simultaneous utilisation of sulphur-containing compounds is provided by the Claus process,[225–227] in which sulphur is obtained using aluminate cements. This process, in particular, uses a wide-pore aluminium-cement catalyst called the Norwegian catalyst.[226] The introduction of the oxides of K, Ba, P, and Ln into catalysts based on high-alumina cements increases the yield of elemental sulphur considerably.[227] A composition containing an alkaline earth metal and aluminium oxide, heated at a high temperature, with S_{sp} = 100–300 $m^2\ g^{-1}$ and a pore volume of 0.30–0.60 $cm^3\ g^{-1}$, has been proposed as an effective sorbent for gases containing SO_x.[228] The extraction of sulphur from SO_2 in flue gases is carried out by reducing the SO_2 with hydrocarbons (CH_4, natural gas) at 450–1300 °C in the presence of calcium aluminates deposited on Al_2O_3.[229]

IX. Catalytic systems for the conversion of CO by water vapour and the synthesis and decomposition of methanol

Copper-containing systems, obtained by deposition, precipitation, or mixing, are extremely effective catalysts for the conversion of CO by water vapour and the synthesis and decomposition of methanol. To maintain the copper-containing component in the active state, it is necessary to use carriers and promoters which are capable of ensuring a uniform distribution of copper in the matrix of stabilising components.

The use of cements has made it possible to obtain catalysts by chemical mixing. The degree of interaction of the components obtained in this way is not less than that obtained by precipitation.

The formation of contact catalysts. The formation of copper-cement contact catalysts has been studied.[52,65,230–233] The catalytic system obtained from copper hydroxide carbonate (CHC) and talyum (CA + CA_2) contains copper hydroxoaluminate, calcium carbonate (as calcite), aluminium hydroxide (as gibbsite), and calcium hydroxide (amorphous to X-rays). The extent of the reaction of CHC with talyum, estimated from the quantities of calcite and gibbsite formed, increases with increase in the fineness of grinding (FG) of talyum, and increases even more strongly with increase in the ratio CA/CA_2.[230,234] The anionic and cationic fractions of CHC have different fates: the carbonate ion is converted into calcite, and the copper ion into copper hydroxoaluminate and $Cu(OH)_2$. At increased temperatures (90 °C), the rate of decomposition of CHC is greater than the rate of its reaction with CA and CA_2; at low temperatures, CA and CA_2 are hydrated slowly, particularly CA_2. On thermal decomposition, copper hydroxoaluminate decomposes to a $CuO-Al_2O_3$ solid solution and CuO. With increase in the heating temperature to 600–800 °C, the spinel $CaAl_2O_4$ is formed from the solid solution. The reactions in the system are described by the general equations (3)–(6). In the three-component CHC–ZHC–talyum system,[230,232] zinc leads to stabilisation of the copper-containing phases and to more uniform distribution of the latter in the catalyst. The two components (ZnO and CuO) are mutually dispersed. Zinc oxide, on the one hand, stabilises copper, and on the other hand competes with it for calcium aluminate, with which they react according to Eqns. (3) and (4). In the two-component CHC–ZHC system, a chemical reaction giving a mixed hydroxide carbonate of Cu and Zn also takes place.[230,232,235] Thermal decomposition gives non-equilibrium solid solutions of Cu^{2+} in ZnO and of Zn^{2+} in CuO; electronic diffuse reflectance spectroscopy (EDRS) detected clusters or associates $(CuO)_x$. In the reduced specimens, an appreciable proportion of the copper is present not as crystallised Cu^0, and the surface of the copper-containing component is increased. Electron microscopy[28] showed that in the $CuO-CaAl_2O_4$ system the disordered copper phase has a globular structure; the introduction of ZnO leads to the formation of a copper phase with a more stable block structure. The thermal decomposition products of copper hydroxoaluminate, namely CuO, the $CuO-Al_2O_3$ solid solution, and then the spinel $CuAl_2O_4$, have a high degree of dispersion, which is preserved up to 600–700 °C.[236,237] A study of the thermal-vacuum electrical conductivity curves.[101,238] established that copper oxide reacts less strongly with the surface of the cements, compared with zinc oxide, and copper has a high surface mobility. A similar study of the CuO–ZnO system[239] detected isolated copper ions and $(CuO)_x$ clusters on the surface, both stabilised by ZnO. In a reducing medium, the copper-cement and nickel-cement systems show an unusual effect of low-temperature decomposition of $CaCO_3$,[125,126] which should lead to changes in the mechanical strength and surface properties of the specimen.

The conversion of CO by water vapour. The conversion of carbon monoxide on highly active copper catalysts at low temperatures makes it possible to decrease sharply the residual concentration of CO and to increase the H_2 concentration. Copper-containing catalysts on a cement base have been used for this purpose.[218,240–244] The NTM catalyst has a high activity at increased pressures.[218] The NTK-10 catalyst subjected to additional treatment[240] has a mechanical strength up to 600–800 kg cm^{-2}, withstands superheating to 300–350 °C, and gives a residual concentration of CO in the converted gas at 200–220 °C close to the equilibrium value. The increase in the strength and degree of compaction of the NTK-10 catalyst at the pressing stage is due to the breakdown of pores with dimensions >300 Å; decrease in the proportion of pores with a radius of 100–200 Å is accompanied by a decrease in the activity.[244] The use of $(NH_4)_2CO_3$ as pore-forming agent in copper-cement contact catalysts alters the porous structure and lowers the activity of the catalyst; this is due to the formation of copper–ammonia–carbonate complexes, which provide a source of copper with an increased ability to undergo recrystallisation.[245] Moist-air and hydrothermal treatment leads to an increase in strength, making it possible to use cement additives to restore the strength of the catalyst and enable it to be used again.[246] The highest activity is shown by catalysts for which the formation of the active phase involves the formation of copper hydroxoaluminate.[65,232,236,237] As finely dispersed CuO separates from the latter (with increase in temperature to 600 °C), the activity increases continuously, after which it decreases sharply as a result of the sintering of copper. For the same reason, the most active contact catalysts are those whose formation involves the reaction of CHC and talyum in the first stage, and the introduction of ZHC in the second:[232] this gives the maximum quantities of copper hydroxoaluminate. In $CuO-Al_2O_3$ and CuO–ZnO solid solutions, copper is converted into an active state ensuring the conversion of CO.[232,235–237]

The mechanism of the low-temperature conversion of CO by water vapour on NTK-10 copper–zinc cement catalysts has been studied.[247–250] The activity of the catalyst is related to its ability to adsorb CO in larger quantities, and H_2O and CO_2 in smaller quantities, on the non-uniform surface.[247] The reaction involves the formation of formate ion by a combined mechanism.[248] The formate complex is produced from CO_{ads} and OH_{ads}; the latter are produced by the dissociative adsorption of H_2O.[249] The temperature of the dissociative adsorption of water provides a criterion of the activity of copper-containing contact catalysts.[250] According to XPES and XAES data,[251] the active species is copper in the Cu^+ state; the zinc maintains copper in this state. A kinetic model of the reaction has been proposed, and the nature of the surface centres responsible for the reaction has been established.[252–254] The limiting stage is the surface reaction of the formate ion with the adsorbed hydroxyl group.

Synthesis of methanol. A large proportion of copper-containing catalysts for the conversion of CO are also active in the synthesis of CH_3OH. This applies to the copper–zinc cement contact catalyst.[218,233] In the synthesis of methanol, as in the conversion of CO, a high activity is shown by contact catalysts containing MHA.[230] A copper–zinc contact catalyst containing hydraulic cement is extremely effective.[255] Cements are also used in other catalysts for the synthesis of CH_3OH at a low pressure.[256]

Decomposition of methanol. Copper–zinc cement catalysts are effective in the decomposition of CH_3OH to CO and H_2.[257] Methyl formate can be obtained by dehydrogenating CH_3OH in the gas phase on a copper-cement catalyst at 150–300 °C.[258,259] The catalyst for the conversion of aqueous CH_3OH by water vapour at 300–600 °C contains group VIII metals, TiO_2, CeO_2, and a Ca aluminate cement.[260]

X. Catalysts for the hydrogenation of oxygen

In various branches of the national economy there is a demand for highly pure gases, in particular gases free from O_2. Gases free from oxygen are required for the hydrogenation of the products of organic synthesis, for example in the production of caprolactam, the hydrogenation of benzene, and the selective and complete hydrogenation of organic compounds. Inert gases free from O_2 are required in chemistry, metallurgy, and other fields. Analysis of data on the purification of technical gases from O_2 [261] showed that the most effective industrial catalysts are Pt, Pd, Cu, and Ni contact catalysts on carriers. The disadvantages of Pt and Pd contact catalysts are their high cost, scarcity, and low mechanical strength. An effective catalyst proposed for the hydrogenation of O_2 contains Ni, Cu, Al_2O_3, $CaCO_3$, and $CaAl_4O_7$;[262-268] this catalyst can operate without breakdown (mechanical strength 300–400 kg cm^{-2}) at temperatures of 100–700 °C and pressures up to 300 atm; the residual concentration of O_2 in Ar is ~0.0007 vol.%. Catalysts for purifying Ar, N_2, and H_2 [263] are obtained by mixing the hydroxide carbonates of Ni (NHC) and Cu (CHC) with talyum in the presence of aqueous NH_4OH solution. The catalyst ensures the removal of oxygen from the gas at oxygen concentrations down to 3.0–3.5% vol. O_2 (this is accompanied by an increase in temperature to 750–800 °C), indicating its high thermal stability and activity. The properties of talyum influence the production of the copper–nickel–aluminium–calcium contact catalyst.[264] Two reduction temperature ranges are observed (300 °C and 540 °C). After high-temperature reduction, the highest activity is shown by the catalyst with the lowest degree of reaction between the components; this may be brought about, for example, by slight preliminary subdivision of the talyum. On the other hand, the catalyst in which the extent of the reaction between the components and the concentrations of Ni and Cu hydroxoaluminates are fairly high shows the highest activity after high-temperature reduction. The possibility of replacing the industrial Pd catalyst AP-1 by the thermally stable and mechanically strong nickel–copper contact catalyst NKO-2 has been examined. Unlike the industrial nickel–chromium catalyst, the NKO-2 catalyst, after being swept with air, is not deactivated and shows no change in its basic characteristics.[265-267] Mixed Ni and Cu hydroxoaluminates provide the starting material for the formation of nickel–copper solid solutions which ensure stability of the active component of the catalysts to the effect of high temperatures and an oxidising medium.[268] The similarity in the reactivities of copper and nickel hydroxoaluminates leads to competition between them in the reaction with talyum. Copper hydroxoaluminate is more reactive.[269] In the NiO–CuO system, a solid solution based on CuO was detected on the surface; the probability of formation of this solid solution increases with increase in the copper concentration and the temperature of treatment.[270]

XI. Catalysts of the Fischer–Tropsch synthesis

Promising methods for the utilisation of coal and natural gas are provided by their conversion into synthesis gas with the subsequent production of hydrocarbons. Aluminium–calcium cements have been used to develop mechanically strong and thermally stable Co and Ni catalysts containing promoting additive (CuO, MgO) for carrying out reactions involving synthesis gas.[271-275] Their selectivity can be altered by varying the composition and conditions of preliminary treatment with hydrogen. Promotion by MgO leads to an increase in the polymerising properties, and modification by copper oxide makes it possible to restrict the growth of the carbon chain to 5–10 carbon atoms. Increase in pressure to 0.82 MPa led to an increase in the yield of liquid hydrocarbons and to the appearance in the products of hydrocarbons with a high melting point (synthetic ceresine).

A distinguishing feature of the mechanism of the production of cobalt–aluminium–calcium contact catalysts, as in the case of other aluminium–calcium catalysts, is the reaction of the components (CA and CA_2) with Co hydroxide carbonate (CoHC), which gives a carrier with a highly developed surface and an active component distributed on the surface. The catalysts show maximum selectivity in the synthesis of liquid hydrocarbons at a degree of reduction of the metal of 65–84%, which requires high-temperature treatment with hydrogen (550 °C).[29] One of the precursors of the catalytically active phase is Co hydroxoaluminate (CoHA),[274,275] which is reduced at 550–650 °C. Modification of the Co catalysts by CuO by the introduction of Cu hydroxide carbonate makes it possible to lower sharply the temperature of the reductive activation of the contact catalysts by 100–150 K and to increase the yield of liquid C_4–C_{10} hydrocarbons.[30,272,276] In the production of the Co–Cu catalysts, a multi-phase system with a highly developed surface (S_{sp} = 170 m^2 g^{-1}) is formed; both components influence the production of the inter-phase boundary.[30] A study of the thermal-vacuum electrical conductivity curves[276] established that CuO forms a solid solution in Co_3O_4, that is Cu cobaltite with variable composition and the spinel structure $Cu_xCo_{3-x}O_4$ ($0 < x < 1$) is produced, and is detected both in the bulk and on the surface. The carrier facilitates the reaction between the oxides and stabilises the surface cobaltite, which is detected even at a CuO concentration of 5% and a temperature of 200 °C. Copper oxide tends to concentrate on the surface of the particles, so that the surface cobaltite is richer in copper than the bulk cobaltite. Cobalt- and nickel-cement contact catalysts containing promoters are regarded as promising catalysts for syntheses based on CO and H_2.[277]

XII. Cement-containing contact catalysts with an acid–base action

The presence of varied acid–base centres in cement-containing catalysts[17,52,61-65,70] strongly suggests that these contact catalysts, in particular the aluminium–calcium catalysts, may be active in the isomerisation of hydrocarbons and the transformation of alcohols even without the introduction of any other elements. The dehydration and dehydrogenation of isopropyl alcohol take place intensively on calcium aluminates with a highly developed surface (galyumins).[52,62,65] The dehydration of the alcohol takes place on a pair of acid–base centres by a two-centre mechanism with the participation of the β-CH-groups of the reagent, and the dehydrogenation takes place on basic centres with the participation of α-CH-groups. The dehydration of α-acetylenic carbinols (prop-2-ynyl alcohol, dimethylethynyl carbinol) [278] also takes place on calcium aluminates by a two-centre mechanism with the participation of acid–base centres. The splitting of α-acetylenic carbinols to give acetylene is an indication of the presence of basic centres. The activity of the catalyst in the splitting reaction increases with increase in the ratio CaO/Al_2O_3. A decrease in the CaO concentration or blocking of the basic centres by the adsorption of an acid intensifies the dehydration of the alcohol. Galyumins

based on aluminium–calcium cements are effective catalysts of the reverse isomerisation of methylacetylene to allene.[279–285] The catalytic isomerisation of methylacetylene provides an accessible method for increasing the supply of allene on an industrial scale. Products based on allene are widely used in various branches of the national economy (dyes, leather, monomers, adhesives, medicines, etc.).[285] The reversible monomolecular isomerisation is described by a first-order equation.[279,282] The maximum value of the specific reaction rate constant is achieved at a definite ratio of the acidic and basic centres in the galyumins; the reaction rate is decreased by both acids (phenol) and bases (pyridine).[279–282] Effective catalytic methods have been developed for obtaining an equilibrium mixture of allene and methylacetylene from pyrolysis gases (methylacetylenic fraction).[283,284]

XIII. Catalytic systems for various organic and inorganic processes

The range of application of high-alumina cements, in particular the alkaline earth aluminates, in catalysis has been increasing continuously in recent years, covering the most varied processes involving the transformation of various nitrogen-, sulphur-, and carbon-containing compounds, from the preparation of the final products to the intensive purification of the effluent gases. The last process is acquiring increasing importance from the ecological viewpoint.

The formation and transformation of nitrogen-containing compounds. A method is known for obtaining oxides of nitrogen by the ionisation of air by a beam of electrons or γ-rays in the presence of calcium aluminates with a highly developed surface (galyumins).[286] The cobalt oxide (Co_3O_4)–calcium aluminate system is an effective and thermally stable catalyst for the oxidation of NH_3;[287–291] the yield of NO at 650 °C is 91.0%.[291] It is suggested[287,289] that $CaAl_2O_4$ actives Co_3O_4. A mechanically strong contact catalyst for the oxidation of NH_3, containing Ca, Al, Fe, and Cr oxides heated at 875–900 °C, has been described.[292] $CaAl_2O_4$ is added to the Fe-containing catalyst for the synthesis of NH_3 to increase its activity.[293] The use of calcium aluminates makes it possible to obtain Fe-containing catalyst blocks for NH_3 synthesis columns with an increased mechanical strength and good operational characteristics.[294] The decomposition of the carbonate component in these contact catalysts[295] takes place as a result of the catalytic action of the highly dispersed metal (Fe). Other metals have a similar effect.[125,126] Intensive enrichment of the surface of the BASF-56-10 industrial catalyst for the synthesis of NH_3 in Al and Ca oxides, which act together as surface promoters, has been described.[296]

Purification of effluent gases from CO. Platinum, rhodium, and ruthenium catalysts on a carrier containing cements and calcium aluminates can bring about the complete oxidation of CO even at room temperature.[297–304] The concentration of calcium aluminates is 35–90%.[299] Calcium aluminates containing 15–35% CaO are used.[300] In addition to Pt and Pd, the addition of compounds of metals of the iron group (Fe, Co, Ni) [305] and also Cu, Ag, Au, Mn, Cr, Sn, and Pb,[306] has been recommended; these contact catalysts are highly stable during use. MnO_2/calcium aluminates are also used to remove CO.[307] The presence of the calcium aluminates makes it possible to carry out the oxidation of CO on these contact catalysts in the presence of SO_2.[308] Fe and Cu oxides are effective promoters of catalysts based on MnO_x and calcium aluminates.[309] Aluminium–copper oxide catalysts with a ratio $Al_2O_3/CuO = 3:1$, modified by Ca, Sr, and Ba aluminates, can be used to oxidise CO at 150–450 °C.[310]

The purification of waste gases. The MnO_2–calcium aluminate catalytic system, which has a fairly high thermal stability, is used to purify spent gases, including exhaust gases, from CO and hydrocarbons.[311–315] Ca silicate and Portland cement can be used as the cement component.[314] Active components of the catalyst, in addition to Mn, are the oxides of Ni, Co, Cu, Fe, and Cr;[316–322] Ba or Sr aluminates are also added in addition to calcium aluminates.[317] The cement component of the catalyst increases its activity and thermal stability.[317] A cement-containing composition has a wide spectrum of action and makes it possible to remove not only hydrocarbons and CO, but also SO_2 and NO.[318,320] Catalysts including metals of the Pt group (Pt, Pd), and also activated carbon and calcium aluminates, have been described.[323–325] A contact catalyst consisting of spinel $M^{2+}M_2^{3+}O_4$ (M^{2+} = Mn, Fe, Co, Ni, Cu, Zn, Ba; M^{3+} = Fe, Al), calcium aluminates, and metal oxides active in oxidation has a high mechanical strength, porosity, and thermal stability;[326] it can be used to oxidise CO, hydrocarbons, SO_2, oxides of nitrogen, aliphatic acids, aldehydes, amines, and other compounds formed in the preparation of foodstuffs. An effective carrier for a catalyst for purifying effluent gases contains Al_2O_3 with added calcium aluminates.[327] An active copper–nickel–aluminium–calcium catalyst, not containing Mn or platinum metals, for purifying exhaust gases has been described.[328]

The catalytic combustion of organic compounds. Catalytic combustion processes are accompanied by strong thermal effects with an increase in temperature, creating severe operational conditions which lead to sintering and the loss of activity by the catalyst. The high melting points of Ca, Sr, and Ba aluminates makes them a suitable base for the production of thermally stable and highly active contact catalysts for catalytic combustion.[74,75,329,330] The sintering of γ-Al_2O_3 is suppressed sharply by adding Ca, Sr, and Ba oxides, capable of forming aluminate structures; a $CoO–BaO–Al_2O_3$ catalyst which has a highly developed surface due to the formation of $BaO.6Al_2O_3$ and which has a high activity in the combustion of CH_4 has been described.[74,75] The dispersion of Mn cations in a Ba aluminate matrix gave a contact catalyst with the composition $BaMnAl_{11}O_x$, whose activity is appreciably greater than that of familiar combustion catalysts such as Pt/Al_2O_3 and $LaCoO_3$.[330]

The partial oxidation of carbon-containing molecules. A highly pure composition containing Al_2O_3 and added barium aluminates, with a low S_{sp} and high mechanical strength, is used in the production of a silver-containing catalyst for the oxidation of ethylene to ethylene oxide.[76] A catalyst consisting of NiO, Al_2O_3, and calcium aluminates is used for the partial oxidation of hydrocarbons.[331] $CaAl_2O_4$ has been proposed as a carrier for a catalyst for the oxidation of C_3H_6 and $(CH_3)_2C=CH_2$ to unsaturated aldehydes and acids.[332] The possible oxidative transformation of CH_3OH to CH_2O over Mo, V, and W oxides deposited on talyum ($CaAl_2O_4$ + $CaAl_4O_7$) has been studied.[333–335] The oxidative dehydrogenation of methanol is accompanied by its oxidation to CO and CO_2, and also by dehydration to $(CH_3)_2O$.

The hydrogenation, dehydrogenation, hydrogenolysis, and alkylation of carbon-containing compounds. The selective dehydrogenation of alkylaromatic hydrocarbons to styrene and its derivatives is carried out on Fe–Cr catalysts containing calcium aluminates, Portland cements, or alumina cement.[336–341] The role of the cements is varied: they increase the selectivity, and act as a binding agent. The introduction of $CaAl_2O_4$ into copper–aluminium and copper–magnesium catalysts for the dehydrogenation of cyclohexanol increases the rigidity of their framework and leads to suppression of the dehydration, increasing the selectivity of the process.[342–344] Aluminium–calcium cement or calcium aluminates with an atomic ratio Ca/Al = 1/(4–10), subjected to thermal treatment at ~1000 °C, after the introduction of Pd are used for the selective hydrogenation of small quantities of more unsaturated compounds (C_2H_2) in the presence of less saturated compounds (C_2H_4).[345,346] The dehydrocyclisation of n-hexane can be carried out on aluminium–chromium–calcium catalysts.[347] The addition of alkaline earth metal oxides, preferably CaO (25%), increases the lifetime, activity, and selectivity of a 0.1–5% Pd/Al_2O_3 catalyst in a single-stage industrial method for obtaining highly pure cyclohexanone by the hydrogenation of phenol at 130–160 °C.[348] The best carrier for the catalyst for the synthesis of stilbene and its derivatives by the oxidative dehydrogenation of toluene and its derivatives in the vapour phase is calcium aluminate or Alcoa-CA-25 aluminate cement.[349–357] During mixing and high-temperature treatment (up to 800 °C), the carrier reacts with the active component; the basic character of the carrier prevents coke formation on the contact catalyst.

The catalytic systems $Ni–Al_2O_3–CaO$, $Ni–Al_2O_3–SrO$, and $Ni–Al_2O_3–BaO$ can be used for the liquid-phase hydrogenolysis of glucose to obtain glycerol and glycols.[358–362] The basic properties of the cement have a positive influence on the process, which takes place preferentially in a medium with a high pH. Since the medium is highly corrosive, it is appropriate to carry out carbonisation of the surface to increase the stability of the contact catalyst. CaO/Al_2O_3, $(CaO + SrO)/Al_2O_3$, and $(CaO + NiO)/Al_2O_3$ compositions have been patented[363] as catalysts for obtaining C_3H_6 from C_4H_{10} at 350–700 °C; the conversion of C_4H_{10} reaches 91%, the yield of C_3H_6 50%, and the ratio C_3H_6/C_2H_4 = 2.7. A catalyst for cracking high-boiling fractions with a large C/H ratio consists of calcium aluminates ($C_{12}A_7$, CA_6, CA, CA_2) and Ba and Sr aluminates, sintered at 1300–1500 °C, with the addition of 0.1–3% of activators (K vanadates).[364] The alkylation of cyclopentadiene and its derivatives by lower alkanols (C_4) is carried out in the presence of basic heterogeneous catalysts, for example a mixture of $Ca(OH)_2$ and Al_2O_3 heated at 1000 °C and treated with water.[365]

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The authors have tried to analyse the principal trends and the most important directions of development of heterogeneous catalysis using cement-containing contact catalysts.

There are grounds for hoping that cement-containing catalysts can be used for the most varied low- and high-temperature processes in organic and inorganic technology. A new research field has now been established, associated with the preparation of oxide and metal oxide mixed cement-containing catalysts. Work is beginning to be developed on the production of deposited cement-containing catalysts. The physicochemical principles of the synthesis of cement-containing catalysts, carriers, and adsorbents for use in gas-phase and liquid-phase processes have been developed, and the regular features of the increase in the strength of their structure at the stages of tablet formation and hydration hardening have been studied. For the preparation of these catalysts, in addition to the already fairly familiar Ca, Sr, and Ba aluminates and high-alumina cements of the talyum type (TU-6-03-339-78), successful use is now beginning to be made of aluminothermal cements such as VTs-70, VTs-75 (TU-21-20-60-84), and also the specially developed high-alumina cement which has been called talyumin (TU-113-03-31-50-88). The physicochemical principles of the preparation of new highly pure high alumina cements have been developed.[9,32]

Cement-containing catalysts are used in more than 100 factories only in the Soviet Union. More than 200 patents covering cement-based catalysts have been published. Assemblies are being developed for the production of cement-containing catalysts by a universal and flexible technology. The use of cement-containing catalysts should help to solve problems of saving raw materials and energy, effectively converting carbon-containing raw material into required end products, protecting the environment, and establishing waste-free industries.

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