DEACTIVATION OF INTERMETALLIDE CATALYSTS IN GAS EMISSION NEUTRALISATION PROCESSES GENERATED BY INDUSTRIAL PLANTS AND VEHICLES

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INTRODUCTION

The catalyst stability and durability have a decisive influence on the economics of emission abatement processes in industrial plants. In this context, the problem of catalyst deactivation in waste gas treatment systems in the huge production volume of industrial enterprises has gained paramount importance. The solution to this problem lies in discovering the nature and regularities of a multitude of phenomena that cause a reduction in the activity, selectivity and service life of catalysts¹.

Until recently, the main problem of catalysis science was the problem of finding catalytically active substances. Today, that problem is the development of a scientific basis for anticipating catalytic action. With the increasing use of catalytic treatment of industrial gas emissions, a very difficult problem arose in studying the nature of changes in the activity of catalysts during their operation, as well as such indicators as increasing the stability and duration of catalysts, extending the duration of cycles, transition from periodic processes with catalyst regeneration to continuous ones, etc. In practice, it has turned out that these indicators mainly decide the fate of the catalyst and the catalytic process of waste gas neutralisation². Losses due to unstable performance and short duration of the catalysts arise primarily due to a reduction in the basic performance of the catalysts and because of the consumption of the catalysts themselves.

The main characteristics of catalysts are known to be activity, selectivity, lifetime and their operating parameters (pressure, temperature, waste gas composition, etc.)³. Reduction of catalyst activity is actually equivalent to

¹ Andreas gremminger, josh pihl, maria casapu, jan-dierk grunwaldt, todd j. toops, olaf deutschmann. pgm based catalysts for exhaust-gas after-treatment under typical diesel, gasoline and gas engine conditions with focus on methane and formaldehyde oxidation. *applied catalysis b: environmental*. 2020. volume 265, 118571.

² Belokon K.V., Belokon Yu.A., Kozhemyakin G.B., Matukhno E.V. Environmental assessment of the intermetallic catalysts utilization efficiency for deactivation of the pollutants emitted by electrode production enterprises. *Scientific bulletin of National mining university*. 2016. Volume №3, Issue 153. Pages 87-94.

³ Renyang Zheng, Zhicheng Liu, Yangdong Wang, Zaiku Xie. Industrial catalysis: Strategies to enhance selectivity. *Chinese Journal of Catalysis*. 2020. Volume 41, Issue 7. Pages 1032-1038.

reduction of power of facilities, reduction of selectivity is equivalent to power overconsumption.

Let us consider two examples of catalyst operation in gas treatment systems. In the first case, the catalyst operates continuously – without regeneration. Here, losses occur due to a gradual decrease in activity and sometimes selectivity. As the activity decreases, it is not uncommon to raise the temperature of the catalytic reactor accordingly to acceptable limits in order to maintain purification at the planned level. This leads not only to higher energy costs, but in some cases also causes a decrease in catalyst selectivity. In this case, of course, a point in time comes when no additional methods can ensure acceptable performance of the catalyst. Then the catalyst reactor or all production has to be stopped to replace the catalyst, which in itself makes a significant contribution to reducing the production of the main product⁴.

In the second case, the slow and irreversible deterioration of the catalyst is overlaid with rapid and reversible changes⁵. Reversible in the sense that the catalyst can be brought back to an active state by regeneration. Regeneration of the catalyst causes production to become periodic, cyclical, consisting of a basic process phase and a catalyst regeneration phase with blowdowns in between.

Turning production into a periodic, cyclic process leads to a dramatic increase in capital and energy costs, complicates apparatus design and maintenance, and in most cases increases the cost of the product.

Many authors⁶ identify additional factors that also reduce the performance of catalysts in gas emission abatement systems. These are the factors responsible for the degradation of the catalyst pellets. In practice, it is often this degradation, rather than loss of catalyst activity, that is responsible for catalyst degradation. Sometimes catalysts are unloaded from the catalyst reactor due to partial failure as this leads to unacceptable increases in catalyst bed resistance and the formation of channels in the dense contact bed, reducing reactor throughput, decontamination rates and dangerous overheating. At the same time, the catalysts unloaded in this state, when tested under laboratory conditions, usually show quite high activity.

Thus, solving the problem of stability and durability of catalysts is one of the most important economic and scientific tasks in the field of catalytic treatment of waste gases.

⁴ Morris D. Argyle, Calvin H. Bartholomew. Heterogeneous Catalyst Deactivation and Regeneration: A Review. *Catalysts*. 2015. Volume *5, Issue* 1. Pages 145-269.

⁵ Delmon B., Froment G.F. Catalyst Deactivation (Studies in Surface Science and Catalysis); Elsevier: Amsterdam, The Nerthelands, 1994; Volume 88.

⁶ Belokon K., Manidina Y., Fedchenok A., Banakh A., Mosiyevych L. The Physical And Mechanical Properties Of Intermetallic Catalysts For The Neutralization Of Carbon-Containing Components Of Emission Gases. *Procedia Environmental Science, Engineering and Management*. 2021. Volume 8, *Issue* 1. Pages 95-102.

1. The meaning and nature of the unstable properties of catalysts

The changes that can occur in catalysts are so diverse and different in nature that the task is to generalise the known cases of catalyst deactivation and classify them.

It should be noted that not all changes in catalysts can be detected, even the most modern methods are sometimes too rough for this purpose and their sensitivity is insufficient, so catalytic activity and selectivity are the most delicate indicators for all changes in the catalyst.

Nevertheless, today there is a very natural scientific basis for the classification of phenomena causing changes in the properties of catalysts. Such a basis is predetermined by the generally accepted measure of catalytic activity (*a*) as the reaction rate of the formation of the target product referred to the unit surface (*S*) of the active phase of the catalyst⁷. Taking into account the degree of utilisation (n) of the catalyst's inner surface, the total activity (*A*) of the catalyst is expressed by the well-known formula:

$A = a \cdot S \cdot \eta$.

It can be seen that changes in the observed activity of the catalyst can be related to changes in the specific activity, specific surface area and the degree of utilisation of the inner surface of the grain. This basis allowed us to systematise the phenomena of changes in catalyst properties in the form of a scheme with a hierarchical structure (Fig. 1). The first, basic level of this structure, is determined by our ideas about the values of catalytic activity (a), specific surface (S) and the degree of use of the inner surface of the grain (η) included in the formula considered. In accordance with this, all phenomena of changes in the properties of catalysts at this level of classification are divided into two large classes. The first class includes phenomena of changes in specific activity or selectivity; the second class includes phenomena of changes in the structure of catalysts, leading to changes in the observed activity due to changes in the size of the working surface or its availability.

⁷ Бєлоконь К.В. Розробка інтерметалідних каталізаторів для знешкодження вуглецевмісних компонентів газових викидів в атмосферу. Монографія. Херсон: ТОВ «Видавничий дім «Гельветика», 2019. 174 с.



Fig. 1. Classification of phenomena causing changes in catalyst properties

The following levels of classification reflect the transition from the most general features to the specific features of individual causes of change. Let us first consider the nature of the phenomena causing changes in the specific activity of catalysts. As can be seen from the classification, it covers the six most common phenomena. Here, the most common cause of changes in catalytic activity and selectivity are changes in the surface and phase composition of the catalyst under the influence of the reaction medium and process conditions, since the chemically interacting systems «catalystreaction medium» must be in equilibrium.

In the vast majority of cases, catalysts are prepared in media other than those of the target catalytic deactivation process. When fresh catalyst is loaded into the reactor, equilibrium is reached during the so-called catalyst development period. The duration and depth of interaction of the catalyst with the work medium depend on their chemical nature and the purification process conditions, and this determines the corresponding period of unstable activity of the catalyst. In this case, the chemical composition of many catalysts can vary in both layer height and grain radius.

A second significant cause of changes in catalytic activity and selectivity is the interaction of the active component with the catalyst carrier. For example, in the catalytic treatment of hydrocarbons, nickel catalysts operate under harsh temperature conditions, undergoing a large number of temperature jumps every day. As a result, after 5–10 thousand hours of operation their activity begins to decline due to the formation in the oxidative environment of the active component compounds with the carrier. When Al_2O_3 is used as a carrier, spinel NiAl₂O₄ is formed. A silicate carrier produces nickel silicates and a mixed oxide (MgNi)O₂ with a magnesium oxide carrier.

A change in the catalytic properties can be caused by changes in the chemical, phase and crystallochemical properties due to chemical interaction and redistribution of the components and also due to crystallographic rearrangements and polymorphic transformations in the catalyst without chemical interaction and exchange with the reaction medium.

In work⁸ that overheating of iron catalyst promoted by potassium, calcium and aluminium leads to its deactivation. This is due to a disturbance of the uniform distribution of promoters, mainly potassium, due to their coagulation with the formation of a new phase. As a consequence, the potassium depletion of the active phase occurs, the chemical composition of its surface changes, which leads to a multiple change in the specific catalytic activity.

It is known that in certain cases, when thermodynamic, mainly temperature conditions are changed, enantiotropic polymorphic transitions of phase modifications may occur. All data indicate that if there is a change in the crystalline state, there should be observed changes in the catalytic properties.

A common cause of reduced catalyst activity is the volatility of the active component or the products of its interaction with the components of the reaction medium.

The phenomenon of catalyst toxicity should be considered as deactivation of catalysts as a result of their interaction with impurities (poisons) contained in exhaust gases with the formation of catalytically inactive or less active in this reaction of chemical surface or volume compounds⁹. In the simplest case of a homogeneous surface, the number of active sites per surface unit (active surface fraction) will decrease when the poison is absorbed. The true specific activity of the surface free of the poison (activity of a single site) and the activation energy do not change in this case. The form of the kinetic equation of reaction does not change either, and the observed activity depends linearly on the amount of poison absorbed.

If the surface is heterogeneous or if the products of the catalyst interaction with the poison also have some activity in relation to the target reaction, a change in the form of the kinetic equation, the activation energy and therefore the true specific activity may be observed. The phenomenon of catalysts poisoning, especially metallic ones (Fe, Ni, Pt, etc.), by sulfur compounds

⁸ Bartholomew C.H. Mechanisms of catalyst deactivation. *Appl. Catal. A.* 2001. Volume 212. Pages 17-60.

⁹ Barbier J. Effect of poisons on the activity and selectivity of metallic catalysts. In *Deactivation and Poisoning of Catalysts*; Oudar, J., Wise, H., Eds.; Marcel Dekker: New York, NY, USA. 1985. Pages 109–150.

contained in the reaction medium is widespread¹⁰. Alkali metal salts have a strong deactivating effect on aluminosilicate catalysts as a result of exchange adsorption and replacement of acidic protons by alkali metal ions, etc.

Coating of the catalyst surface with active precipitates formed from raw materials partially or completely shields the active surface of the catalyst, changing the measurable catalytic activity and selectivity.

The most common causes of changes in catalytic activity are reduction of crystal defects and crystallisation and sintering of catalysts.

Industrial catalysts are usually highly dispersed porous bodies with a developed surface, the presence of crystal lattice micro-distortions – atomic shifts from regular positions in the lattice, excess vacancies, etc¹¹. Therefore they are systems removed from thermodynamic equilibrium. Therefore catalysts gradually undergo irreversible structural changes in the process of operation: the specific surface decreases, the total porosity and in some cases the catalyst volume decreases, etc.

The slow decline in activity of catalysts due to changes in structure is commonly referred to as ageing¹².

Crystallisation and sintering, although related, are nevertheless different processes. Crystallisation of catalysts leads to crystal growth and ordering of the whole structure with the elimination of defects and distortions in the crystal lattice. The process is predominantly driven by surface diffusion. As a result, the smallest particles disappear, pore size increases and the surface decreases. However, the total pore volume, size and apparent density of the catalyst granules change insignificantly. During crystallisation a relatively stable and more homogeneous ordered structure is formed, which is characterised by certain crystal sizes.

The sintering process also leads to the disappearance of small pores. Volumetric diffusion plays an important role in sintering, with small crystals fusing together in an irregular manner. Sintering is a process of random compaction of the system with shrinkage of the structure and the formation of agglomerates of various sizes. In this case, an unstable structure is formed that tends to further densify due to crystallisation, which can then proceed during the operation of the catalysts.

The activation energies of the crystallisation and sintering processes are different. In the lower temperature range there are mainly crystallisation and

¹⁰ Rostrup-Nielsen J.R. Promotion by poisoning. In *Catalyst Deactivation (Studies in Surface Science and Catalysis)*; Bartholomew, C.H., Butt, J.B., Eds.; Elsevier: Amsterdam, The Nethelands. 1991. Volume 68. Pages 85–101.

¹¹ Sereda B., Belokon Y., Belokon K., Kruglyak I., Sereda D. Modeling of the processes of obtaining porous materials under SHS conditions. *Materials Science and Technology*. 2019. Pages 1331-1335.

¹² Чейлитко А.О., Белоконь К.В., Жеребцов О.А., Носов М.А. Формування пористих структур інтерметалідних каталізаторів. Монографія. Запоріжжя: ЗДІА. 2018. 208 с.

structure ordering processes. With increasing temperature predominantly sintering is accelerated.

The question regarding the relation of these processes and especially their quantification is poorly developed: however, even purely qualitative concepts in this regard have led to very significant results for more thermostable catalysts. On the basis of such insights, it was concluded that in cases where disperse catalysts require precalcification, it is necessary to choose a regime that would cause preferably a process of crystallisation and ordering of the structure rather than sintering. Such a pre-crystallised catalyst will largely lose its tendency to sintering and will have increased thermal stability and durability.

A third cause of change in the structure of the catalysts is a change in the dispersed structure of the deposited active ingredient. This refers mainly to the behaviour of catalytically active metals on the surface of the carrier (Ni, Pt, Ag, etc.)¹³.

The specific surface area of the deposited active ingredient and thus the activity per unit weight grow with an increase in dispersity. But at the same time the recrystallisation and sintering stability of the system decreases noticeably. It is precisely this circumstance that gives rise to a large number of studies. The coarsening of deposited active ingredient particles is mainly influenced by high temperatures.

The stability of the deposited component depends not only on its physical properties, but to a large extent on the nature of the carrier and the strength of the bond with it.

The most common cause of changes in activity and sometimes selectivity is catalyst coking¹⁴. When catalysts get coked, they are usually regenerated. However, it is clear that the need to regenerate catalysts makes the process either periodic or requires circulation of the catalyst between the reactor and regenerator. Both of these greatly increase the entire cost of the gas purification process. The catalyst is thus subjected to enormous additional chemical, thermal and mechanical stress and, as a consequence, many of the above causes of irreversible catalyst activity loss due to recrystallisation, phase composition changes, etc.

Another cause of catalyst deactivation is contamination by mechanical impurities that may be contained in the feed¹⁵. The mechanical impurities deposit on the surface of catalysts, clog the mouths of their pores, block the active surface and thereby reduce its availability for the reactants.

¹³ Russo N., Salahub D.R. Metal-support interaction in catalysis, in *Metal-Ligand Interactions in Chemistry, Physics and Biology.* Springer Netherlands, Dordrecht. 2000.

¹⁴ Pio Forzatti, Luca Lietti. Catalyst deactivation. *Catalysis Today*. 1999. Volume 52, Issues 2–3. Pages 165–181.

¹⁵ Larsson, Ann-Charlotte. Study of Catalyst Deactivation in Three Different Industrial Processes, Acta Wexionensia No 106/2007, 2007. 59 p. Written in English.

Finally, last but not least, a phenomenon that leads to catalyst degradation is the mechanical destruction of the catalyst. Mechanical and abrasion resistance is one of the characteristics regulated in catalyst specifications. In some cases, this characteristic becomes decisive and determines the fate of catalysts¹⁶.

The classification reveals the variety of phenomena leading to changes in catalyst properties in their unity and relationship to specific catalysts, systematises and groups these phenomena according to their common nature, reveals general regularities within each group of phenomena and guides us to study each such phenomenon with all its specificity in order to make targeted recommendations for any industrial catalyst.

These recommendations may concern changes in catalyst preparation technology or even their chemical or phase composition, changes in development conditions, regeneration or operating regimes, raw material requirements, etc.

The conclusions to be drawn from the above are that it is necessary to:

1. To intensify research of the nature of the phenomena reducing efficiency and service life of catalysts in order to:

a) make recommendations on how to prepare more stable working catalysts;

b) make recommendations for catalyst operating regimes, especially for development stages, regeneration and other extreme cases.

2. To raise the engineering level of catalytic treatment to exclude all deviations in regimes that reduce catalyst quality in reactor operations (overheating, leakage, corrosion, hydrodynamic shocks, poisoning, etc.).

3. To provide production with better equipment for all stages of catalyst production that would allow for an optimum overall production regime. It concerns the equipment connected with sedimentation, autoclaving, calcination, energy-stressed milling, moulding, pelletising, etc.

4. To increase work on implementation of fundamentally new methods and techniques in technologies of catalyst production, which allow to create more stable and durable catalysts.

5. To provide production of catalysts with qualitative raw materials and chemicals which would guarantee the highest quality indicators of catalysts and minimize side effects, especially coking, recrystallization, inhibition, etc.

6. To increase requirements for waste gases entering the catalytic reactors or catalytic converters for purification, thus excluding poisoning and other harmful phenomena.

¹⁶ Dongfang Wu, Lingya Song, Baoquan Zhang, Yongdan Li. Effect of the mechanical failure of catalyst pellets on the pressure drop of a reactor. Chemical Engineering Science. 2003. Volume 58, Issue 17. Pages 3995-4004.

7. To extend works on kinetics of catalyst deactivation, mathematical modelling and optimization of processes taking into account regularities of catalyst properties changes.

8. To strengthen works on development of express methods for determination of catalysts operation stability taking into account nature of the phenomenon which decreases catalysts efficiency in off-gas cleaning processes, etc.

2. Development of promising intermetallide catalysts for the neutralization of gas emissions from industrial enterprises and vehicles

The high degree of toxic component conversion in the cleaned gases has made precious metal-added catalysts widespread around the world, consuming more than 40 tonnes of platinum alone per year to produce. The main disadvantage of such catalysts is their high cost due to the price of the neutralisation set as well as insufficient thermal and toxic resistance, which stimulates scientific research aimed at creation of more economically and technologically optimal compositions and methods of preparation of catalysts¹⁷.

One promising direction in this area is the development of polymetallic catalysts based on intermetallides of transition metals⁷. Numerous literature data indicate that doping of polymetallic catalysts enhances the catalytic activity and, to a certain extent, thermal stability¹⁸. One of the reasons for increased catalytic activity is considered to be the distribution of functions between the individual surface active centres of the catalysts. It is known that the binding energy of oxygen to the oxide surface has a decisive influence on their activity in oxidation reactions. The acceleration of one process, such as activation on Pd atoms, leads to the increase of electron concentration in the catalyst and facilitates the acceptor stage of the process – oxygen activation on metal oxides with the formation of oxygen ions. Thus, a number of authors discovered¹⁹ that cobalt and copper oxides doped with Pd and Pt exhibit

¹⁷ Belokon K., Belokon Yu., Matukhno E. Development of Scientific and Technical Decisions for Increasing Environmental Safety of Cleaning Processes from Carbon-containing Components of Gas Emissions. XIX International Scientific Conference «New Technologies and Achievements in Metallurgy, Material Engineering and Production Engineering», Collective Monograph, Nr 78, Częstochowa. 2018. Pages 44–48.

⁷ Белоконь К.В. Розробка інтерметалідних каталізаторів для знешкодження вуглецевмісних компонентів газових викидів в атмосферу. Монографія. Херсон: ТОВ «Видавничий дім «Гельветика», 2019. 174 с.

¹⁸ Belokon K., Manidina Y., Fedchenok A., Matukhno E. Development of method for catalytic purification of carbon-containing components of gas emissions from industrial enterprises. *Procedia Environmental Science, Engineering and Management*. 2019. Volume 6. Issue 4. Pages 545–552.

¹⁹ Debing Li, Xianhong Liu, Qinghong Zhang, Ye Wang, Huilin Wan. Cobalt and Copper Composite Oxides as Efficient Catalysts for Preferential Oxidation of CO in H₂-Rich Stream. Catalysis Letters. 2009. Volume 127. Pages 377–385.

extraordinary activity in oxidation reactions of carbon oxide and hydrocarbons.

A promising way of manufacturing catalysts for neutralization of exhaust gases of industrial enterprises and internal combustion engines is the method of powder metallurgy under thermochemical interaction of components to form new phases of intermetallic type^{20,21}.

For many catalytic reactions, it is possible to use cheaper materials and methods of their production. They include catalysts based on FeAl intermetallic with a Ranay structure (the Ranay structure is formed as a result of leaching Al from FeAl intermetallic, in which only Fe remains, which has a branched structure).

Intermetallic compounds, or intermetallides (from the Latin inter – between and metal), are chemical compounds of two or more metals with each other:

Me_mMe'_n,

where Me and Me' are metals;

m, n - stoichiometric coefficients.

Fe, Co, Ni, Cu, Cr, Mo, Si, Al, Mg and other metals can be used as a basis for the production of intermetallide catalysts.

To investigate the possibility of using cheaper contacts in catalytic converters or neutralizers, we chose polymetallic (intermetallide) catalysts based on iron with additives of cobalt, manganese and copper. The choice of these systems was based on a number of considerations, such as the exclusion of precious metals; high activity in deep oxidation processes used in industrial gas treatment systems; high strength and heat resistance, which is very important for contacts used in catalytic converters; wide application in various industries and a good production base for mass producing of polymetallic catalysts.

In this regard, it was decided to research FeAl intermetallides when used as catalysts for the complete oxidation of hydrocarbons and carbon dioxide contained in the waste gases of industrial plants and internal combustion engines. Iron and aluminium can form intermetallics: FeAl₃, Fe₂Al₇, Fe₂Al₅, FeAl₂, FeAl, Fe₃Al. The systems based on Fe-Al intermetallide of the stoichiometric composition FeAl₃, synthesized by the thermal spontaneous combustion method, were used as the catalysts under investigation. In order to increase the catalytic activity, the intermetallides were modified with different amounts of cobalt, manganese, and copper²².

²⁰ Belokon K., Belokon Yu. The usage of heat explosion to synthesize intermetallic compounds and alloys. *Ceramic Transactions*. 2018. Volume 261. Pages 109–115.

²¹ Belokon, K., Pohrebennyk, V., Sybir, A., Manidina, Y., Banakh, A. Optimal composition of intermetallic catalyst for neutralization of carbon containing components of gas emissions. Procedia Environmental Science, Engineering and Management. 2021. Volume 8, *Issue* 1. Pages 79–86.

²² Belokon K. Developing of polymetallic catalysts for neutralization of carbon-containing components of gas emissions from vehicles. В кн.: Європейський вектор модернізації економіки в умовах сталого розвитку промислового регіону Київ: Інтерсервіс. 2021 С. 361-373.

The systems based on Fe-Al intermetallide of the stoichiometric composition FeAl₃, synthesized by the thermal spontaneous combustion method, were used as catalysts for the oxidation of carbon monoxide and hydrocarbons.

In order to increase the catalytic activity, $FeAl_3$ intermetallide was modified with different amounts of cobalt, chromium, manganese, and copper in amounts up to 15 wt%. Appropriate mixtures of powders with a dispersion of 100-150 μ m were used as a reaction medium.

The powder mixtures were prepared by the method of double-sided pressing in a collapsible mould with a floating piston to obtain cylindrical blanks.

The production of intermetallide catalysts by thermal spontaneous combustion was carried out at an installation consisting of the following main functional systems: reaction equipment, gas supply system, system for monitoring and controlling technological parameters, and gas utilisation system²³.

The production of catalysts by the thermal spontaneous combustion method included dosing, mixing, mould filling and pressing of a cylindrical billet with a diameter of 20 mm and a height of 20 mm with a relative density of 0.5. The dispersion of the powders was 100-150 μ m. The pressing force was varied in the range of 30-100 kN.

The resulting workpiece was placed in a hot pressing matrix, filled with an inert medium, and heated evenly. Even heating results in self-heating of the workpiece.

Due to the exponential dependence of the reaction rate on temperature, the temperature rise in the workpiece volume proceeds with progressive self-acceleration and ends with a sharp temperature jump, initiating the process of spontaneous combustion, as a result of which high-temperature synthesis starts in the mixture. During thermal spontaneous combustion, high sample temperatures are reached almost simultaneously in the entire workpiece due to self-heating. After the combustion wave passes, the workpiece is held at a temperature of 390-460°C for 0.5-1 hour. At the heat treatment stage, the resulting product is finalised. The main feature of this method is that the combustion process is initiated not from the surface, but by heating the entire volume of the reactant to the combustion temperature. Depending on the ratio of the defining parameters, the maximum temperature can occur either in the centre of the reaction volume or between the centre and the surface.

In general, the chemical scheme for the preparation of multicomponent intermetallide compositions by the thermal spontaneous combustion method can be presented as follows:

²³ Белоконь Ю.О., Белоконь К.В., Жеребцов О.А. Спосіб отримання інтерметалідного сплаву: патент № 133598 України, 2019.

 $(Ox_1 + Ox_2 + Ox_3 + ... + Ox_n) + R \rightarrow [Multicomponent alloy] + RkOl+Q,$ where: Ox_n – metal oxides; R – reducing metal (Al); [Multicomponent alloy] – in this case (Fe, Co, Mn, Cu)Al_x; Q – thermal effect of the process.

As a result of the high combustion temperatures, the synthesis process itself is very short-term and usually takes several tens of seconds. As the aluminium content in the synthesized alloys increases, the phase separation of the metal and oxide phases worsens, so the experiments were carried out under the influence of high mass fields (overload) generated in a centrifugal unit.

This method of synthesis allows obtaining a separate intermetallide phase, as well as one applied by impregnation to a specially added granular or porous monolithic carrier.

The synthesis products for all the studied compositions were an ingot consisting of two layers: the lower one was an intermetallide alloy based on Co, Mn, Cu and Fe aluminides and the upper one was an oxide material based on Al_2O_3 (corundum). With complete phase separation, the lower metal layer was easily separated from the upper one after a slight mechanical impact.

The sample obtained in the form of a stack was then crushed and sieved. For catalytic studies, a fraction with a particle size in the range of 400-600 μ m was selected for each of the obtained systems.

The modified samples were prepared from pre-dried metal powders by mechanical mixing.

The resulting metal ingots were crushed and then classified to the desired fraction of 0.1-0.3 mm. The powder fraction was classified using sieve analysis. The choice of this fraction was determined by the design of the catalytic converter filter and its operating conditions.

At the next stage, the classified alloy particles were transferred for chemical treatment (alkaline leaching).

The skeletal catalyst was obtained by leaching 1 g of the obtained intermetallide with various acids and alkali. Then the catalyst was thoroughly washed from traces of alkali by washing with water and ethyl alcohol.

The catalyst is prepared by removing aluminium from the intermetallide precursor by etching with a 20% aqueous solution of NaOH or KOH, followed by removal of the remaining hydrogen with a hydrogen peroxide solution.

The alkali solution was taken in excess of the amount required to remove aluminium from the precursor. The sample was either poured into the alkali solution or submerged in small portions and kept for 30 minutes at room temperature, and then boiled for an hour. After that, the sample remained in the solution for another day at room temperature. After 24 hours, the alkali solution was poured off and the samples were treated with a 10% hydrogen peroxide solution to remove residual hydrogen from the catalyst surface and stabilize the sample. The treatment of the catalyst with hydrogen peroxide also increases its activity. The catalyst was then washed on a filter with distilled water until the reaction was neutral. The samples were then dried in an oven at $120^{\circ}C^{22}$.

Aluminium was removed from the intermetallide by the following reaction:

 $MAl_x + xNaOH + 3xH_2O \rightarrow M + xNaAl(OH)_4 + 3x/2H_2\uparrow$.

The amount of aluminium removed was controlled by the weight loss of the sample. Further, the composition of the catalyst will be characterised by numbers showing the mass ratio of transition metals included in the charge for the preparation of intermetallides. Losses at all stages of the synthesis do not exceed 5%.

X-ray studies of the reaction products were performed on a DRON-3 diffractometer using monochromatized CuK α -radiation in the range 20 = 20-60°. The content of active components was determined by atomic absorption spectroscopy. The surface area of the catalysts was measured by BET-thermal argon desorption on a Sorpty device (Carlo Erba, Italy).

The activity of the synthesized catalysts was studied in the reactions of carbon monoxide oxidation and deep oxidation of propane on a flow-through unit with chromatographic analysis of reaction products (Porapak Q).

Installation consists of a cylindrical flow reactor with turning gas flow, representing two quartz tubes inserted into each other with inner diameter of 15 mm with a catalyst layer, 10 mm thick on a fibrous substrate, thermocouple to control temperature in the reactor, chromatograph (gas analyzer), flow meter and a tank with a model gas mixture. The catalyst is predominantly heated by the flow of the model gas mixture heated at the outer walls of the reactor. Loading of the catalyst of 0,1-0,3 mm fraction was 1 cm³ at relative volume rate of gas flow W = 11 250 h⁻¹. The model gas mixture consists of 0,2 vol.% propane, 0,5 vol.% carbon monoxide (II), 1,3 vol.% oxygen (this corresponds to an oxygen excess ratio $\alpha \approx 1,0$) and nitrogen up to 100%.

The reaction products were passed through a desiccant to remove the water formed during the reaction. The experiments were performed in the temperature range from 100 to 500°C, depending on the activity of the catalyst, with an interval of 25-100°C.

The catalytic activity was characterized by the temperature of 100% CO conversion ($T_{100\%}$).

²² Belokon K. Developing of polymetallic catalysts for neutralization of carbon-containing components of gas emissions from vehicles. В кн.: Європейський вектор модернізації економіки в умовах сталого розвитку промислового регіону Київ: Інтерсервіс. 2021 С. 361-373.

The catalysts obtained from iron-based intermetallide precursors exhibited sufficiently high catalytic activity. However, oxidation on them has a number of features that are not characteristic of other catalysts.

These catalysts have a higher specific surface area and, according to X-ray phase analysis, consist mainly of oxides. Let us consider in detail the process of CO oxidation on catalysts derived from FeA1₃ and FeA1₃-CoAl₃ precursors. All samples, except for the latter, did not undergo hydrogen peroxide treatment in the process of preparation, so a large amount of hydrogen is adsorbed on their surface. This explains their high activity in the first experiment. Hydrogen, burning out, gives a significant increase in temperature in the reactor. This is no longer observed in the second experiment, so the temperature of 100% conversion according to the above curves can be determined with a sufficient degree of accuracy. The sample Fe (100%) starts working only at 200°C and full conversion of CO on it is reached at 500°C. But when cobalt is added to the composition the activity of catalysts increases sharply. Already 5% of wt.% of cobalt give practically full conversion of CO at 350°C. The sample with 15 wt.% cobalt shows the best result – full conversion of CO is reached at 250°C²⁴.

Hydrogen peroxide treatment allows not only removal of hydrogen chemisorbed at leaching from catalyst surface, but also increases its activity. On the sample treated with hydrogen peroxide and containing 15% wt. cobalt 100% conversion of CO is achieved at 200°C.

Propane conversion on this series of samples goes the same way as CO conversion with increase of activity depending on increase of amount of cobalt. The best result is shown by catalyst sample with 15% wt. cobalt treated with hydrogen peroxide. Propane conversion on it reaches 75% at 350°C.

The peak of activity in the propane conversion curve on Fe (100%) catalyst may be related to the fact that hydrogen formed in the leaching process is more firmly bound to the catalyst surface and desorbed at higher temperature than on other catalysts.

Since the addition of manganese significantly increases the activity of intermetallide catalysts, it was decided to add it as well to the iron and cobalt catalysts. All catalysts were pretreated with hydrogen peroxide. The cobalt content in the samples was constant at 15 wt.% and the manganese content varied from 6 to 15 wt.%.

Such samples show activity in CO oxidation already at 100°C, which is not typical for other intermetallide catalysts. At the best sample containing 12 wt. % manganese a full conversion of CO is reached at 200°C. Oxidation

²⁴ Belokon K. Intermetallic catalysts development to reduce emissions of motor vehicles through catalytic disposal of pollutants. 4nd International Scientific and Technical Internet Conference «Innovative development of resource-saving technologies and sustainable use of natural resources». Petroşani: UNIVERSITAS Publishing, 2021. Pages 86–88.

of propane on iron-cobalt catalysts with manganese content is more active with increase of its quantity up to 15 wt. %. The most active sample with 15 wt.% Mn gives 100% conversion of propane at 350°C.

Studies of catalytic activity of samples with the addition of Cu showed their significant differences from the previously studied catalysts.

Fe-Co-Mn-Cu catalyst (67%-15%-15%-3%) in the first experiment shows rather high activity in deep oxidation reactions. At 200 °C it completely burns CO, at 300 °C – propane.

According to the analysis of data on the primary catalytic activity of freshly prepared catalysts (table 1) it can be concluded that the addition of Cu increases the catalytic activity of catalysts.

Table 1

Catalyst composition	Fe-Co (85%-15%)	Fe-Co-Mn (70%-15%-15%)	Fe-Co-Mn-Cu (67%-15%-15%- 3%)
Temperature of 100% CO conversion	250	250	200
Temperature of 100% propane conversion	Over 350	350	300

Comparative characteristics

The iron-based samples show activity in CO oxidation at lower temperature. On the main mass of samples the conversion of CO begins already at 100°C. However, this high activity negatively affects the stability of these catalysts.

The catalyst that has lost its activity does not contain a metallic phase and consists entirely of oxides. The catalysts Fe 100 % and Fe-Co with different content of cobalt sharply lose activity in the oxidation of CO and propane after the first experiment, and after the second it is almost equal to zero in the temperature range under study.

Addition of manganese also positively affects the activity of iron-based catalysts. Various Fe-Co-Mn catalysts behave quite similarly. During the first five experiments their activity in oxidation of CO and propane does not change. Then a gradual slow decrease follows, but within ten experiments it reaches a level of about 1/3 of the original activity.

Additional alloying of Fe-Co-Mn catalysts with copper leads to formation of strong bonds between grains in the catalyst, which increases the strength limit of the catalyst and increases its working time in gas purification systems. At the first ten experiments their activity in oxidation of CO and propane does not change, then follows a gradual slow decrease by 15-18 %, then takes a gradual value.

3. Deactivation of ultradisperse metallic catalysts in gas-phase processes

Ultradisperse metallic catalysts (skeletal, carrier catalysts, etc.) are widely used in chemical, petrochemical, medical and a number of other industries, as well as in waste gas purification systems^{25,26}. They have a well developed surface, high grain and sub-grain boundaries, they are characterised by significant defect concentrations, the presence of micro-, super-micro– and narrow mesopores and, as a consequence, metastability and tendency to recrystallisation processes, in relatively mild conditions. The mechanism of such catalysts formation was investigated by many authors. Fundamentally important, determining their structure and performance characteristics are 3 stages:

1. Breaking of metal-ligand bonds in initial compounds where ligands can be oxygen atoms, anions, organic radicals or metals which can be selectively removed by treatment with strong electrolytes.

2. Occurrence of new metal-metal bonds, polynuclear clusters and microcrystals of catalytically active phases.

3. The aggregation of these primary elements with the formation of a porous body, on the accessible surface of which the reactant molecules are further activated.

This scheme, of course, reflects only the most general features of the mechanism of genesis of catalysts with a highly developed surface.

Each system is characterised by specific features depending on the nature of the initial substances and the conditions for preparing the catalysts. For example, the mechanism of formation of Renay catalysts has not been clearly established so far. In the literature²⁷ 3 alternative mechanisms are discussed – volumetric and surface diffusion and solution-sedimentation. The most probable of them is the first one, but the contribution of the other two cannot be completely excluded in most cases.

In the selective corrosion of multicomponent alloys, the initial phases break down and their constituents rearrange in accordance with the state diagrams of metallic, oxide and hydroxide systems. Most of the modifying additives in the course of catalyst genesis undergo chemical transformations with valence changes and, migrating along the solid– electrolyte interface, form metal-oxide agglomerates with active phase particles. Real catalysts are complex associations of metal particles and epitaxial layers, amorphous or weakly crystallised oxides,

²⁵ Rumiantsev V., Yakubin N., Bielokon K., Matukhno E., Leventsova C. Ecological aspects of the neutralization of gas emissions leaving from the resin storehouse of Joint-stock company «Zaporozhkoks». *Metallurgical and Mining Industry*. 2015. Volume 7, *Issue* 4. Pages 105–109.

²⁶ Belokon K. Environmental aspects of neutralization of gas emissions from chemicalrecovery production. International scientific and practical conference with the participation of young scientists «Sectoral problems of environmental safety – 2022». Kharkiv: Kharkiv National Automobile and Highway University. 2022. Pages 6–8.

²⁷ Bakker, M.L., Young D.J., Wainwright M.S. Selective leaching of NiAl₃ and Ni₂Al₃ intermetallics to form Raney nickels. J. Mater. Sci. Volume 23, *Issue* 11. 1988. Pages 3921–3926.

spinels, undissolved intermetallides, bronzes of non-stoichiometric composition and hydrides. They contain base and alloying metals in various degrees of oxidation. Topochemical reduction reactions of these compounds in the presence of metals that easily activate hydrogen play an important role.

One of the reasons for deactivation of such catalysts in the course of operation is their transition to thermodynamically stable states.

Deactivation of iron, nickel and a number of other metal catalysts by oxidation is slowed by the presence of adsorbed and dissolved hydrogen on their surface and in the volume. The state and localization of hydrogen in Fe-Reney have been investigated by a variety of methods. The methods of inelastic neutron scattering and diffraction, electron microdiffraction and mass spectrometry of secondary ions proved to be the most informative in solving this problem. It turned out that there is no «deep», structural or dissolved hydrogen in Fe-Renay: all of it is in the adsorption layer on the catalyst surface. During the genesis of Fe-Renay, thin layers of iron hydride are formed at the «alloy-electrolyte» interface due to the formation of hydrogen during the dissolution of aluminum, which spontaneously decomposes during catalyst storage.

The ageing and deactivation of Renay catalysts during storage are caused by several processes: oxidation of the most energy-saturated surface areas, recrystallisation, coagulation and coalescence of metallic, oxide and hydroxide phases, segregation of components, etc. To understand the mechanism of these processes was possible by combining traditional integral methods of research (X-ray diffraction at small and large angles, thermogravimetry, electron and neutron imaging) with local methods (scanning and transmission electron microscopy with microdiffraction X-ray microanalysis) and methods to determine the valence state of elements, the nature of the bonds between them and the nature of the immediate surroundings. The deactivation of ultradispersed metal catalysts under the influence of high temperatures is mainly due to their recrystallization. It proceeds most intensively in a hydrogen atmosphere, to a lesser extent in an inert and oxidizing environment.

Thermal treatment of catalysts due to a reduction in the number of centres with high coordination unsaturation, a change in the orientation of crystallographic faces and lattice deformation due to gas diffusion into the metal volume is usually accompanied by a change in the character of energy inhomogeneity of their surfaces.

The specific catalytic activity of catalysts increases in this case due to the preferential annihilation of micro– and super-micropores that do not contribute appreciably to the total activity of the catalyst. The true constant of the reaction rate per unit of an equally accessible surface remains unchanged,

and the observable one, on the value of which the specific catalytic activity is calculated, is symbate to the efficiency factor.

The evolution of heterogeneous catalysts under the action of the reaction system is a consequence of the formation and disintegration of labile adsorption complexes leading to the reconstruction of the surface layers of the solid, changes in its chemical composition, phase transformations and segregation of components. In a vacuum, the catalyst surface is enriched with components with minimal sublimation heats and in the reaction medium with maximal chemisorption heats. Each composition of reaction mixture and temperature corresponds to a certain steady state of the catalyst, independent of its initial state. The deactivation kinetics of heterogeneous catalysts and the relaxation time depend on the surface layer reconstruction mechanism and the process conditions. The disintegration kinetics of agglomerated structural elements of heterogeneous catalysts depends on the reaction heat.

Despite the complexity of deactivation phenomena in real catalytic processes, changes in the morphology and structure of catalysts during operation play a crucial role in many cases. For example, a comprehensive study of a iron catalyst that had been in operation for 2400 hours showed that the decrease in activity was due solely to iron crystal growth and a reduction in the available surface area. All other factors (carbonization, poisoning, change of chemical composition, etc.) do not have any noticeable effect.

Among many reasons that cause deactivation of catalysts on carriers, a special role belongs to the effect of strong interaction of the active phase with the substrate. It is accompanied by a change in the valence of the metal, the shift of electron density in the system, and in extreme cases – the formation of new chemical compounds.

Metal catalysts are also affected by poisoning due to the degradation of a number of organic compounds to form strongly adsorbed particles or carbonaceous deposits. Regeneration of such catalysts is based on removal of coke layers blocking the active surface by oxidation at high temperatures. Organic decomposition products can also be removed by anodic or cathodic polarization of the catalysts.

In order to create metallic catalysts that are stable in long-term operation, it is necessary to introduce micro additives of oxides and hydroxides that are difficult to regenerate and localise in the form of thin interlayers at the grain boundaries. Such interlayers slow down recrystallization of ultradisperse catalysts. For the first time it was proved on the example of the fine powder of platinum modified by hydroxides of alkaline earth metals. Structuralforming oxides may be introduced into fine-dispersed powder of VIII-group metals by modification of charge for the oxidative melting or during decomposition of bifunctional reducing agents: hydrides, borohydrides, aluminohydrides, carbonyls, haloid carbonyls and salts of variable valence metals (Ti³⁺; V²⁺, Fe²⁺, etc.). Similar role is played by oxides in skeletal catalysts. Thus, for example, Fe-Renay of FeA1₃ containing almost no aluminum hydroxides intensively recrystallizes already at relatively low temperatures (Fig. 2).



Fig. 2. Dependence of specific surface area of skeletal iron catalysts and leaching temperature

In contrast, catalysts with significant amounts of aluminium oxides and hydroxides and alloying additives retain a highly developed surface even under the most severe leaching conditions.

In Fe catalysts Renay leached under mild conditions, $A1(OH)_4$ is most amorphous and decomposes at low temperatures. Such catalysts sinter intensively (Fig. 3). As the degree of crystallinity of the hydroxide phase increases, they become much more stable.



Fig. 3. Change of specific surface area of Fe-catalysts during annealing. Leaching conditions: 1 – 96° C, 20% NaOH, 1 hour; 2 – 20° C, 20% NaOH, 1 hour; 3 – 20° C, 20% NaOH, 2 hours

The examples discussed in this paper are not the only variants of catalyst deactivation phenomena. In real processes, it is most often caused by more than one factor.

The differential clarification of their role using a set of modern research methods and knowledge of the general principles of stabilisation of ultradispersed metals is a rational basis for creating catalysts that are stable in long-term operation.

CONCLUSIONS

1. The problem of catalyst deactivation in waste gas treatment systems of industrial enterprises and motor transport has now become of paramount importance. The solution to this problem lies in revealing the nature and regularities of many phenomena that cause a reduction in the activity, selectivity and lifetime of catalysts. A decrease in catalyst activity is actually equivalent to a decrease in unit capacity, a decrease in selectivity is equivalent to an overconsumption of power.

2. Classification of the phenomena causing changes in the properties of catalysts has been developed. The phenomena causing changes in properties of catalysts are divided into two classes. The first class includes six phenomena of changes in chemical composition of an active surface of catalysts resulting in a change of specific activity or selectivity. The second class also includes six phenomena of alterations in the structure of catalysts that result in changes in the observed activity due to a change in the size of the working surface or its accessibility.

3. In the first class the most common causes of changes in the catalytic activity and selectivity are: changes in the surface and phase composition of the catalyst under the influence of the reaction medium and process conditions, interaction of the active component with the catalyst support, changes in the chemical, phase and crystallochemical properties due to chemical interaction and redistribution of components, and also crystallographic remodelling and polymorphic transformations in the catalyst without chemical interaction and exchange with reaction medium, volatility of the active ingredient or products of its interaction with components of the reaction medium, poisoning by poisons, coating of surfaces by active precipitates formed from raw materials.

4. The main reasons for changes in the structure of catalysts are: changes in the dispersed structure of the deposited active component, coking, sintering, reduction of crystal defects and recrystallisation, contamination by mechanical impurities, mechanical destruction.

5. A skeletal catalyst based on FeAl₃ intermetallide with Rhenay structure synthesized by thermal self-ignition was developed for use in gas emission purification systems. The skeletal catalyst was obtained by liquifying the obtained intermetallide with various acids and manganese with the subsequent removal of the water content by aqueous peroxide solution. Catalyzers obtained from intermetallic precursors on the basis of iron showed rather high

catalytic activity. They have more high magnetic surface and, according to X-ray diffraction analysis, are composed of oxides.

6. The main reasons of intermetallide catalysts deactivation were studied. They include: transition of catalysts into thermodynamically stable states, recrystallization, carbonization, poisoning, change of chemical composition, etc.

SUMMARY

The paper considers the main issues of intermetallide catalysts deactivation in waste gas emission treatment systems of industrial enterprises and motor vehicles. The classification of phenomena causing changes in the properties of catalysts is given. It is shown that the phenomena causing changes in the properties of catalysts are divided into two large classes. The first class includes phenomena of changes in the chemical composition of a catalyst active surface resulting in a change in the catalyst specific activity or selectivity. The second class includes phenomena that change the structure of catalysts and cause a modification of the observed activity due to a variation in the size of the working surface or its accessibility. This classification systematises and groups all the phenomena according to the generality of their nature and reveals general regularities within each class of phenomena. A skeletal catalyst based on FeAl₃ intermetallide with the Renay structure has been proposed for use in gas emission treatment systems. A method of obtaining the intermetallide catalyst by thermal spontaneous combustion followed by leaching has been described. The main causes of deactivation of intermetallide catalysts were studied. These include: reduction of specific surface area, change in porous structure, change in phase and chemical composition, recrystallization, carburization, poisoning, etc.

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