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Chemical Design of Binary TWC Catalysts for Conversion of NO_x, CO and Hydrocarbons

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Abstract

It has been found that thermal decomposition of binary complexes of composition $[Co(NH_3)_5Cl][M^*Cl_4]$ (M^* = Pt и Pd) and $[M(NH_3)_x][M^*Cl_y]$ (M = Cu, Ni) that have been obtained for the first time can be used to produce binary catalysts with uniform distribution of active components. The procedure of the controlled formation of multipurpose zones on the surface of $Pt{-}Ni/\gamma\text{-}Al_2O_3$ and $Pd{-}Co/\gamma\text{-}Al_2O_3$ catalysts has been developed, which significantly increases their activity. As a consequence of the study into the conversion of gas mixture on these catalysts, the possibility for segregative interaction of NO and CO has been found. It has been demonstrated that a non-additive increase in catalytic activity of binary catalysts is caused by oxygen depassivation of Pt and Pd centres owing to spillover of oxygen that is formed during NO decomposition. The mechanism of the spillover of oxygen has been suggested, the sense of which consists in the realization of a new reaction path of slightly bonded states of adsorbates.

INTRODUCTION

To neutralize products of combustion of hydrocarbon fuel, the use is made of three-functional (Three Way Catalysts, TWC) Pt/Rh catalysts that provide a simultaneous conversion of CO, hydrocarbons, and nitrogen oxides. In view of the permanently decreasing level of admissible concentration of toxic components in the spent gas and in view of the expanding field of TWC application, creation of new compositions of catalysts, *i.e.* their chemical design, becomes a topical problem. In spite of an intensive search for alternative energy sources, the volume of the injection of toxic products of the combustion of hydrocarbon fuel in the atmosphere will not tangibly go down in the near future. The optimal solution for this environmental problem is catalytic conversion of spent gases.

The basis of modern-day TWC catalysts is formed by inert monolithic (cellular) cordierite blocks ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$), and less often, by metal (fechral) blocks with the internal walls of their channels coated with stabilised $\gamma\text{-}Al_2O_3$ that is impregnated by a mixture of platinum and rhodium (~5 : 2). The mass of the platinum metals in the converter comprises 1–2 g depending on the volume of the catalyst. Cordierite cellular blocks show small specific surface (less than $0.1\ m^2/g$); therefore, to increase the surface, a layer of $\gamma\text{-}Al_2O_3$ (20–60 μm) is applied onto the walls of the block channels. The optimum pore size for the reaction to proceed in the diffusion field (~200–350 °C) comprises 10–100 Å; however, $\gamma\text{-}Al_2O_3$ transforms to $\alpha\text{-}Al_2O_3$ with the decrease in the specific surface up to $1{-}5\ m^2/g$ over the region of ~1150 °C. To suppress this process, stabilizers, specifically, La_2O_3, ZrO_2 *etc.*, are added in the pulp during the application of a secondary carrier.

Currently, the works are under way into the creation of a TWC catalyst on the basis of Pt + Pd or Pd-containing compositions alone, which is caused by the limitation of rhodium resources. In order that these catalysts be used in practice, it is necessary to reduce passivation of active sites by oxygen that is formed during the neutralization of NO_x, to reduce the reaction temperature, to suppress thermal degradation of materials, to afford a possibility for a "dry cleaning" of the catalyst, not to complicate the regeneration process for platinum metals in the converters that have served their lifetime, *etc.*

TWC catalysts must possess a high selectivity and at the same time, they must increase the speed of several different reactions:

$CO + 1/2O_2 \Rightarrow CO_2$ (1)
Hydrocarbons $+ O_2 \Rightarrow H_2O + CO_2$ (2)
$H_2 + 1/2O_2 \Rightarrow H_2O$ (3)
$NO + CO \Rightarrow 1/2N_2 + CO_2$ (4)
$NO + H_2 \Rightarrow 1/2N_2 + H_2O$ (5)
Hydrocarbons $+ NO \Rightarrow N_2 + H_2O + CO_2$ (6)
$NO + 5/2H_2 \Rightarrow NH_3 + H_2O$ (7)
$CO + H_2O \Rightarrow CO_2 + H_2$ (8)
Hydrocarbons $+ H_2O \Rightarrow CO + CO_2 + H_2$ (9)
$3NO + 2NH_3 \Rightarrow 5/2N_2 + 3H_2O$ (10)
$2NO + H_2 \Rightarrow N_2O + H_2O$ (11)
$2N_2O \Rightarrow 2N_2 + O_2$ (12)
$2NH_3 \Rightarrow N_2 + 3H_2$ (13)

(This is exactly what their important and unique feature consists in.)

The catalyst must be very active, as the time for its contact to gas varies from 100 to 400 μs. The selectivity of a TWC catalyst has to manifest itself in its capability to promote the reaction (1), (2), and (4)–(6) earlier than (3). In addition, the reactions (4) and (5) must precede the reaction (7) *etc.*

The stage of NO dissociation on an active site of a platinum metal is very important in complex multistage reaction $NO + CO \rightarrow 1/2N_2 + CO_2$. This occurs most readily on rhodium, and worse, on Pt and Pd. Adding Pt and Pd enhances the oxidizing activity of the catalyst, but gives rise to ammonia in the case of the combustion of a rich mixture (that is enriched by hydrocarbons in comparison with the stoichiometric composition).

We supposed that multiphase catalysts with various functional zones can stimulate simultaneous passing of several reactions. As is known, the activity of the mixed contacts appreciably depends on the way of their obtaining.

In this connection, of interest are the obtaining and the investigation of these model multiphase catalysts, where it is possible to assess the behaviour of each of these components. This approach can be considered as chemical design of a tailor-made material. Until now, an empirical search for these materials occurred most often, for example, for TWC catalysts that provide a preassigned state of various components on the surface.

The work in this direction in the Institute of General and Inorganic Chemistry (IGIC), Russian Academy of Sciences, has begun in 1992 under the initiative of Yu. A. Buslaev. Experts from various laboratories, institutes, and factories took part in the work from the very beginning. Owing to such cooperation, not only significant results have been received in the field of inorganic chemistry and catalysis, but also the task in view has been solved in practice: a new type of the effective automobile catalyst has been created.

As is known, catalytic properties of the obtained materials can be changed to a large measure through the modification of the ceramic substrate. By the example of $Pt-Ni/\gamma\text{-}Al_2O_3$ and $Pd-Co/\gamma\text{-}Al_2O_3$ systems, we have found that the substrate is involved in the process of the reaction when a strong electronic interaction with the platinum metal appears. In this relation, the procedures for metallization of a ceramic substrate have been designed. The processes of nickel plating and cobalt plating appeared to be the most promising for practical implementation.

As a consequence of the research of $Co(Ni)-NH_3-H_2O$, $Co(Ni)-N_2H_4-NH_3-H_2O$, $Co(Ni)-(NH_2)_2CS-NH_3-H_2O$ and $Co(Ni)-N_2H_4-(NH_2)_2CS-NH_3-H_2O$ systems, it has been found that upon heating of hydrazine-ammoniac solutions ($pH > 12$) that contain Co^{2+} and Ni^{2+} to 80 °C, metallization of the solid phase that is in the solution occurs. The reaction rate rises within the first hour, which is indicative of an autocatalytic nature of the process. Adding

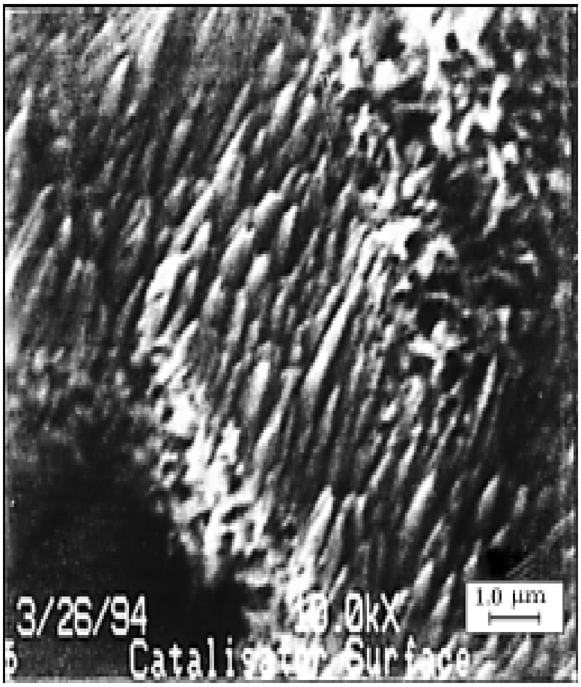

Fig. 1. Photomicrograph of a nickeled substrate from γ-Al_2O_3. The needles are metal nickel.

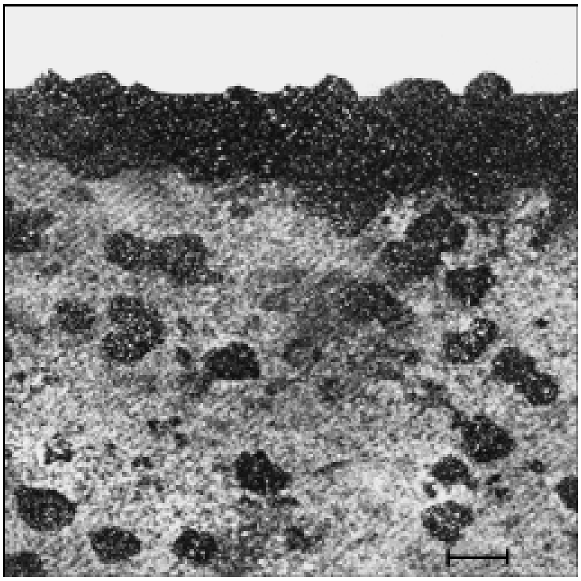

Fig. 2. Photomicrograph of $[Co(NH_3)_5Cl][PdCl_4]$ that is synthesized in γ-Al_2O_3 superficial layer (a sectional view across the height of the layer).

thiourea to hydrazine-ammoniac solution has an effect of cobalt and nickel reduction even at ambient temperature (15–25 °C), which makes it possible to obtain coatings without additional activation (Fig. 1). It has been found that chemical metallization occurs with involvement of SO_2^- ion-radical that is formed as a result of thiourea oxidation. Optimum parameters of the process have been determined. New methods for nickel plating and cobalt plating of ceramic and metal substrates have been developed (and patented) on the basis of this reaction.

BINARY Pt(Pd)-CONTAINING COMPLEXES, THE PRECURSORS OF BINARY CATALYSTS

An effect of synergism that consists in a superadditive increase in the activity of the catalyst has been detected in the study of catalytic activity of Pt and Pd that have been applied onto a nickel- or cobalt-metallized substrate from γ-Al_2O_3. Interpretation of the results has been performed with the use of binary catalysts that have been obtained in thermal decomposition of binuclear complexes of compositions $[Co(NH_3)_5Cl][MCl_4]$ (M = Pt and Pd) и $[M_1(NH_3)_x][M_2Cl_y]$ (M_1= Cu, Ni; x is equal to 4 and 6 for Cu(II) and Ni(II), respectively; M_2 = Pt, Pd; y is equal to 4 in the complex of Pt(II), Pd(II), and 6, in that of Pt(IV)). Depending on the medium, the thermolysis of binary complexes enables obtaining of ultrafine solid solutions or multiphase compositions.

The possibility to synthesize slightly soluble binary complexes in pores of a substrate (Fig. 2) with the subsequent thermal decomposition allows their use as the intermediate compounds to yield new catalysts.

CO OXIDATION BY NITROGEN MONOOXIDE ON Pt–Ni AND Pd–Co BINARY CATALYSTS

As is known, decomposition of nitrogen monooxide on platinum metals is preceded by dissociative adsorption of NO. This process includes the following unit steps: $NO + 2Z \leftrightarrow ZN + ZO$ and $2ZN \rightarrow 2Z + N_2$ where Z is the adsorptive centre. While the recombination desorption of N_2 is "instant", the desorption of oxygen in the absence of a reducer is perceptible only at high temperatures (> 500 °C), *i.e.* a decrease of the catalyst free surface that is accessible for NO_x occurs. The adsorbed oxygen can be eliminated from the surface by means of increasing the concentration of a reducer, but the air/fuel ratio (λ) is a constant magnitude in modern cars. An alternative path of oxygen depassivation is a controlled generation of the texture of the surface so that the migration of oxygen is provided from the active sites, where the dissociation of NO occurs, to the active sites where the oxidation of CO and hydrocarbons will take place. Such bifunctional system (an atom of a platinum metal and another centre with a coordinated active oxygen) is thought of as a promising one in the development of new, rhodium-free TWC catalysts.

It has been found in the study of the conversion of NO + CO mixture that the conversion level of nitrogen monooxide is higher for Pd–Co/γ-Al_2O_3 sample, and the temperature of the beginning of the process of CO and NO conversion is lower than for Co/γ-Al_2O_3 and Pd/γ-Al_2O_3 samples (Fig. 3).

The nature of the conversion of nitrogen monooxide on Pt–Ni/γ-Al_2O_3 sample significantly differs from that for Pt/γ-Al_2O_3 and partly repeats the process on Pd–Co/γ-Al_2O_3 catalyst. First of all, synergism manifests itself in significant decrease of the temperature range of the reaction. Accordingly, the process of NO reduction on Pt–Ni begins at 75 °C, and amounts to as much as 50 % at 150 °C, whereas on Pt/γ-Al_2O_3 sample, at 100 and 170–200 °C, respectively. Substantial growth of the oxidizing activity of the bimetallic sample is of particular interest. During the study of the samples by the XRE method, a negative chemical shift for metallic platinum and palladium has been detected. The shift manifests itself in that a significant decrease (by ~1 eV) of binding energies of metallic Pt 4*f* 7/2 and Pd 3*d* 5/2 is evidenced after catalytic decomposition NO → O + N in XRE spectra of all model samples we have investigated. A circumstance should be particularly noted that atomic oxygen is formed (during the decomposition of nitrogen monooxide) on these metals under the test conditions, this oxygen, conceivably, passivating them, and a positive shift of the binding energy must be observed.

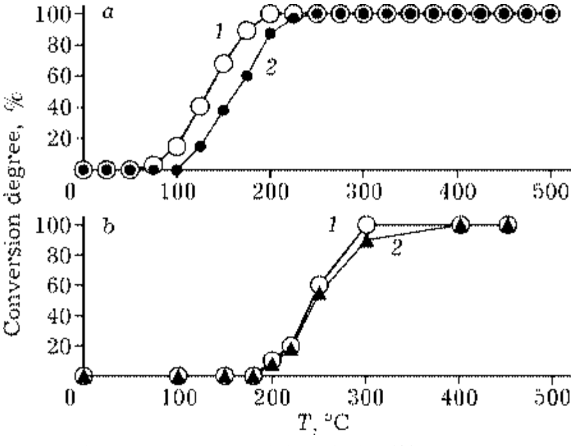

Fig. 3. Conversion of NO *(1)* and CO *(2)* as a function of the temperature on Pd–Co/γ-Al_2O_3 (*a*) and Pd/γ-Al_2O_3 samples (*b*). The composition of the gas mixture: 1 vol. % NO + 1 vol. % CO + 98 vol. % He.

It appears that the negative chemical shift is caused not by a local transfer of electronic density, but by a modification of the electronic structure of superficial centres and by a decrease in their coordination number. It was found that this effect appears when two conditions are complied with: multiphase nature of the composition and the possibility of electronic exchange with a substrate. The acquired results allow the suggestion that the processes of recombination of nitrogen atoms with the desorption of nitrogen molecule (gas chromatography data) and those of oxygen migration from Pt(Pd) atoms to atoms of a non-platinum metal occur after catalytic decomposition of nitrogen monooxide on Pt(Pd) atoms. The interphase diffusion (spillover) of the adsorbed oxygen must result in a decrease of the coordination number of the active sites of platinum metals, and hence in a negative chemical shift in XRE spectra (exactly as it was observed). The emergence of loosely bonded oxygen on an alternative phase must lead to a segregative interaction of the catalyst with NO and CO. To put it another way, in the case that this path of the reaction is realized, oxygen depassivation of platinum will occur with simultaneous and substantial growth of the oxidizing activity of the contact, i.e. with an increase in the activity of the catalyst both with respect to NO and to CO. It was this effect (synergism) that we observed in the experiments and that consisted in a superadditive increase of the activity of catalysts.

To prove the spillover of oxygen, BaO was used with the capacity for capturing the oxygen that migrates over the surface and for stabilising it in the form that is suitable to be investigated by the EPR method. The interaction of Pd/BaO with NO has been studied in a wide interval of temperatures. It has been found that upon the treatment at the temperature of catalytic decomposition of nitrogen monoxide, the sample shows an EPR-spectrum that is typical for BaO_2 with the parameters of the spin Hamiltonian $g_{II} = 2.024$ and $g_{\perp} = 2.002$. According to literary data, these values of g-factors are not typical for radical speciations of oxygen on Pd and they cannot be assigned to adsorbed NO molecules. By virtue of the fact that barium oxide is catalytically inactive with respect to NO, the formation of BaO_2 is possible only in the case of migration (spillover) of oxygen that is formed upon NO decomposition on Pd.

The results arrived at in the research make it possible to explain the reason for the activation of palladium (platinum) in the mixed contact we have obtained. Oxygen that is formed during the conversion of NO is adsorbed on palladium in the case of Pd/γ-Al_2O_3, whereas in the case of Pd–Co/γ-Al_2O_3, it is formed on palladium and then it migrates to cobalt. This phase must become the site for reoxidation of the surface: $O + 2e^- \rightarrow O^{-2}$. However, it is improbable that the addition of two electrons occurs by a single elementary act. Most likely, it is realized through several stages:

$2O(Pd) \rightarrow 2O(Co^{+n})$

On alternative metals, the involvement of the adsorbed radicals of oxygen can be presented as follows:

$2O(Co^{+n}) \rightarrow Co^{+(n+1)} + O_2^-(ads.)$

$O_2^-(ads.) + CO \rightarrow CO_2$

$O^- + Co^{+(n+1)} \rightarrow Co^{+n} + O$

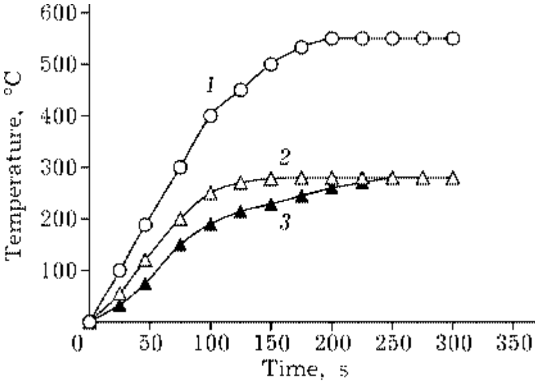

Fig. 4. Variation of the temperature from the moment when the engine starts: in the spent gas before an inlet to the cellular block (*1*), in the metallized (*2*) and in the non-metallized (*3*) cellular ceramic blocks.

Superficial oxygen radicals possess a uniquely high reactivity. So, it is well-known that the O^- anion-radicals react with CO even at the temperature of liquid nitrogen. The expected route of the reaction makes possible to assume the spillover of oxygen arising in the conversion of nitrogen monooxide.

Studying the Pt–Ni/γ-Al_2O_3 TWC catalyst with the metallized ceramic substrate has revealed a number of its essential advantages. First of all, this is an increase in the heating rate of the ceramic block from the moment when the engine starts (Fig. 4), *i.e.* cutting-down the time for a “cold start” that is one of the requirements of Euro-3 specifications.

Figure 5 displays the results of testing of Pt–Ni/γ-Al_2O_3 catalyst under LEV specification (USA) with the use of a car with a 1.8 l engine. It is evident that full conversion of all toxic components of the spent gas (NO_x, CO, and hydrocarbons) occurs in 2 min after a cold start-up.

We have performed the assessment of the efficiency of the converter during the neutralization of spent gases on the basis of stand and driving tests of various cars,

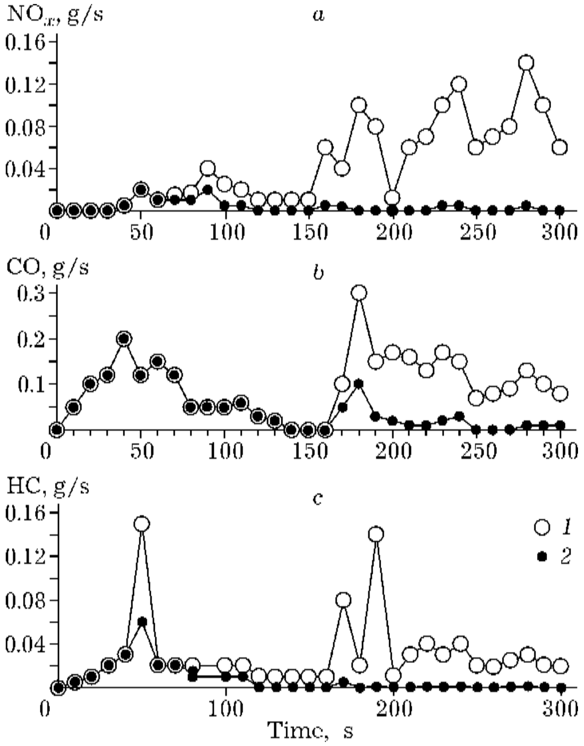

Fig. 5. Variation of the content of NO_x (*a*), CO (*b*), and hydrocarbons (*c*) before (*1*) and after (*2*) the use of Pt–Ni catalyst.

TABLE 1

The results of the tests that have been performed in NAMI into the toxicity of pre-production models of catalytic blocks around a ceramic carrier in the case of neutralizer as a constituent of the neutralization system for the VAZ-2112 car according to the UNECE Regulations No. 83

Serial number of the tests	Emissions of harmful substances				Dimensionality of the emissions of harmful substances	Drive cycles
	CO	CH	NO_x	CH + NO_x		
	Tests in accordance with ECE15 + EUDC drive cycle with a prior warm-up of the engine (40 s) (for normalization of Euro-1 (2))					
Test 1 (cold)	1.044	0.211	0.202	0.413	g/km	B type (ECE15 +EUDC)
	52.4			17.4	Euro-2	Toxicity margin, %
	Tests in accordance with ECE15 + EUDC drive cycle without prior warm-up of the engine (for normalization of Euro-3 (4))					
Test 2 (cold)	1.38	0.162	0.166	–	g/km	B type (NEDC)
	40	19	10.6		Euro-3	Toxicity margin, %
	Tests with the warmed up engine					
Test 3.1 (hot)	5.21	1.17	2.13		g/test	A type (ECE15)
	0.815	0.145	0.145		g/km	B type (ECE15 + EUDC)
Test 4.2 (hot)	3.59	0.833	2.08		g/test	A type
	0.651	0.118	0.343		g/km	B type
Test 5.3 (hot)	2.459	0.736	1.104		g/test	A type
	0.548	0.101	0.170		g/km	B type
Specifications	2.72		0.97		g/km	Euro-1
of the UNECE	2.2		0.5		g/km	Euro-2
Regulations No. 83	2.3	0.2	0.15		g/km	Euro-3

including UAZ-3160, “Knyaz’ Vladimir”, VAZ-21073, VAZ-2110, and VAZ-2112 (Table 1).

CONCLUSION

Thus, we have created new multipurpose Pt–Ni and Pd–Co binary catalysts for the conversion of NO_x, CO, and hydrocarbons. The ways for layer-by-layer application of active components have been suggested for the first time and the procedures to produce the appropriate TWC catalysts have been developed. It has been demonstrated that the use of a metallized ceramic substrate raises the activity of the catalyst and reduces the time for its “cold” start-up. The developed approaches of chemical design have made it possible to obtain a new type of low-temperature converter of NO_x, CO and hydrocarbons. Comparative tests of pre-production models of the converters have confirmed that their efficiency (the degree of neutralization, time for a “cold” start, the content of platinum metals, the width of λ-zone) is significantly higher than that of the known commercial samples.

Acknowledgements

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