# Effect of a Structure–Size Factor on the Catalytic Properties of Complex Oxide Compositions in the Reaction of Deep Methane Oxidation

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Received October 11, 2005

**Abstract**—The following catalysts for deep methane oxidation were studied using X-ray diffraction analysis, scanning electron microscopy, transmission electron microscopy, temperature-programmed reduction with hydrogen, and temperature-programmed ammonia desorption: highly dispersed supported aluminum—manganese and cobalt–zirconium catalysts; bulk and supported nanosized spinel ferrites. It was found that structure–size factors in complex oxide nanocomposites are responsible for differences in the catalytic properties (activity and thermal stability). The efficiency of the supported ferrite and cobalt–zirconium catalysts depends on both the oxygen–catalyst bond strength and the acid properties of catalyst surfaces.

**DOI:** 10.1134/S0023158407030111

## **INTRODUCTION**

The development of energy generation by the flameless catalytic combustion of methane is one of the most promising areas in current fundamental and applied catalysis. In this case, unlike torch combustion, 95-100% methane oxidation to CO<sub>2</sub> occurs at temperatures lower than 800°C; this significantly increases the efficiency of the process and provides an NO<sub>x</sub> emission level of about 1 ppm. The absence of efficient low-temperature catalytic systems with high performance characteristics hinders the widespread use of the catalytic combustion of gaseous hydrocarbon fuel. Supported platinum and palladium catalysts are the most active catalysts for the deep oxidation of methane. However, because they are expensive, there is a need for the development of new low-temperature catalysts without noble metals.

The deep oxidation reactions of hydrocarbons, in particular, methane, on catalysts containing noble metals are structure-sensitive; that is, the rate of these reactions depends on the particle size of the active component [1, 2]. The determination of the role of the structure-size factor in changing the catalytic properties of oxide systems opens up new additional opportunities for the development of less expensive catalysts for deep methane oxidation with controllable characteristics. In this work, we synthesized various nanosized complex oxide systems and tested them in the deep methane oxidation reaction. The following test systems were studied: aluminum oxide catalysts modified with rare earth (REE) and alkaline earth elements (AEE); the cobaltzirconium oxide systems Co<sub>x</sub>O<sub>y</sub>//ZrO<sub>2</sub> and Co<sub>x</sub>O<sub>y</sub>//(ZrO<sub>2</sub>zeolite), including Rh- and Pd-promoted systems; and bulk and supported ferrites with the spinel structure  $M^{II}Fe_2^{III}O_4$  (M is Mn, Co, or Ni) modified with surfactant additives.

# **EXPERIMENTAL**

Supported aluminum oxide catalysts. The supported aluminum oxide catalysts were prepared by the treatment of supports with the supersaturated solutions of active metal salts (barium nitrate, strontium nitrate, lanthanum nitrate, copper nitrate, cobalt nitrate, chromium nitrate, and manganese acetate) under nonequilibrium conditions at an elevated temperature (method I) [3, 4] and by the traditional impregnation of supports with a mixture of soluble metal salts followed by drying and calcination (method II). The total metal content of a catalyst was 10-12 wt %: 5 wt % Mn (Cu, Co, or Cr), the balance being lanthanum, barium, and strontium modifying additives. The cobalt content of an unmodified cobalt catalyst was 10 wt %. Rare earth and alkaline earth oxides were chosen as modifying additives because of their ability to disperse fusible oxides of transition metals, in particular, manganese ( $T_{\rm m} = 535-1080^{\circ}$ C), and to stabilize low-temperature Al<sub>2</sub>O<sub>3</sub> modifications at overheating temperatures. Commercial A-1 and ShN-2 alumina samples and Al<sub>2</sub>O<sub>3</sub> prepared by a sol-gel method, which provides an opportunity to obtain fine-powder materials with a particle size to 2-4 nm [5, 6], were used as supports. Aluminum hydroxide was prepared by the neutralization of a solution of  $Al(NO_3)_3$ with a solution of NH<sub>4</sub>OH to pH 9–10 followed by washing the resulting precipitate to remove  $NO_3^-$  (reaction with diphenylamine). The pressed precipitate as a hydrogel was treated in an autoclave at  $150^{\circ}$ C for 6 h. The resulting transparent sol was dried at  $60-80^{\circ}$ C until the precipitation of Al(OH)<sub>3</sub>, which was then calcined in air at  $600^{\circ}$ C.

**Bulk spinels.** The bulk spinels were prepared by coprecipitation from corresponding metal nitrate solutions with an aqueous solution of sodium hydroxide at a specified value of pH followed by keeping the suspension at room temperature. The resulting suspensions were filtered; the precipitates were washed to a negative reaction for  $NO_3^-$  and dried at 110°C in air; thereafter, they were calcined at 700°C for 7 h.

Note that homogeneous complex oxides are difficult to prepare by methods commonly used for the preparation of spinels, for example, the coprecipitation of hydroxides from corresponding metal salt solutions. The spinels thus prepared are usually characterized by low specific surface areas; they are inhomogeneous and contain impurities that impair their physicochemical properties [7, 8]. Surfactant additives can be used in order to control the particle size of complex oxides [9]. According to patent data [10], bulk spinels, including those modified with surfactant additives (to 6 wt % carboxymethyl cellulose), were prepared by the thermal decomposition of the trinuclear heterometallic iron acetate complexes  $[Fe_2^{III} M^{II}O(CH_3COO)_6(H_2O)_3] \cdot 2H_2O$ (where M<sup>II</sup> is Mn, Co, or Ni). The advantage of this method is that it provides an opportunity to obtain nanosized complex oxides with controllable composi-

Supported spinel catalysts. The supported spinel catalysts were prepared by the decomposition of presynthesized trinuclear transition metal carboxylate complexes in porous support matrices [10]. Commercial ShN-2 alumina and zirconium dioxide modified with yttrium oxide (7 wt %  $Y_2O_3$ ) were used as supports [12]. The  $Y^{3+}$  cation was introduced into a support for the low-temperature stabilization of a cubic ZrO<sub>2</sub> modification, which is characterized by a smaller particle size, as compared to a monoclinic modification. The addition of the Y<sup>3+</sup> cation resulted in the formation of vacancies in the oxygen sublattice of ZrO<sub>2</sub>; this facilitates its crystallization in a cubic form [13]. Catalyst samples were also prepared by mechanically mixing ferrites presynthesized from carboxylate complexes with a support  $(\chi - Al_2O_3)$ . The ferrite content was 4–6 wt %.

tions and particle sizes [11].

**Cobalt–zirconium oxide catalysts.** The cobalt–zirconium oxide catalysts were prepared by coprecipitation and impregnation. The ( $Co_xO_y$ –ZrO<sub>2</sub>) sample was prepared by the coprecipitation of cobalt and zirconium hydroxides with an aqueous ammonia solution from cobalt and zirconium nitrate solutions at pH 9. The resulting suspensions were filtered; the precipitates were washed until the washings were free of NO<sub>3</sub><sup>-</sup>. The washed and pressed precipitate, which was shaped into small cylinders and dried at room temperature (xerogel), was subjected to hydrothermal modification, which provides an opportunity to regulate the pore structure of the coprecipitated systems over a wide range and, in a number of cases, facilitates the formation of fine crystalline phases with high specific surface areas [14]. The modification was performed in an autoclave with saturated water vapor at 150°C for 6 h. After the hydrothermal treatment, the xerogel was dried at 150°C and calcined at 400°C for 5 h.

The supported samples were prepared by the impregnation of supports with a cobalt nitrate solution under nonequilibrium conditions at an elevated temperature followed by drying at 100°C and calcination at 350°C for 6 h. Reagent grade ZrO<sub>2</sub>, zirconia modified with yttrium oxide (7 wt % Y<sub>2</sub>O<sub>3</sub>) [12], zirconium dioxide prepared by a sol-gel method, the H form of synthetic pentasil zeolite TsVN (HTsVN), and the binary system [65% ZrO<sub>2</sub> (sol-gel)-35% HTsVN] were used as supports. The last-named binary system was synthesized in accordance with a published procedure [15] in the following manner: A zeolite suspension was added to an aqueous suspension of a zirconium hydrogel, and the mixture was intensely stirred for 45 min to reach higher homogeneity. Next, the sediment was pressed, dried at 100°C, and calcined at 500°C for 3 h. The catalysts based on the binary zeolite-containing support were promoted with Rh and Pd additives (0.5 wt %) using the solutions of palladium nitrate and rhodium chloride (RhCl<sub>3</sub>  $\cdot$  4H<sub>2</sub>O) followed by drying and calcination. The concentration of cobalt oxide in all of the samples was 10 wt % (on a metal basis).

The phase composition of catalysts and supports was determined by X-ray diffraction (XRD) using a DRON-3M diffractometer (Cu $K_{\alpha}$  radiation;  $\lambda = 1.54184$  Å). The average size of crystallites was determined from the Scherrer equation [16]. The specific surface area ( $S_{sp}$ ) of samples was measured using the thermal desorption of argon. The pore structure of particular samples was characterized based on the results of methanol adsorption (desorption) in a gravimetric system equipped with a McBain–Bakr quartz helix balance. The samples were preevacuated ( $P \sim 10^{-2}$  Torr) at 330°C. The total pore volume was evaluated from an adsorption isotherm at  $P/P_s = 0.98$  assuming that pores are filled with a condensed liquid adsorbate.

The redox properties of catalysts and supports were studied by temperature-programmed reduction (TPR) with hydrogen over the range 20–900°C at a heating rate of 10 K/min in a flow system equipped with a trap with molecular sieves (-50°C) to remove water. The amount of hydrogen consumed for the reduction of a catalyst was measured by chromatography (thermalconductivity detector). The flow rate of a 10% H<sub>2</sub> mixture in Ar was 50 cm<sup>3</sup>/min. The catalysts were preheated at 250°C in a flow of argon (30 cm<sup>3</sup>/min) for 1 h.

The surface acid properties of samples were studied by temperature-programmed ammonia desorption



**Fig. 1.** The temperature dependence of methane conversion on modified manganese catalysts prepared using method I (a) before and (b) after treatment at 900°C. Catalyst supports: (1) A-1 (method II), (2) A-1, (3) ShN-2, (4)  $Al_2O_3$ (sol-gel).

(TPAD) in accordance with a procedure described elsewhere [15].

The electron-microscopic study of particular samples was performed with the use of scanning and transmission electron microscopes (REM-100U and JEOL JEM 100 CX-II, respectively).

The catalytic activity of samples (1 cm<sup>3</sup>; particle size of 1–2 mm) was characterized by the conversion of CH<sub>4</sub> into CO<sub>2</sub> (which was determined in a quartz flow reactor at atmospheric pressure and a space velocity of 6000 h<sup>-1</sup> using a gas mixture containing 1% CH<sub>4</sub> in air) and the temperature at which a 10 or 80% methane conversion was reached ( $T_{10}$  or  $T_{80}$ , respectively). The starting substances and reaction products (CH<sub>4</sub>, CO<sub>2</sub>, and CO) were analyzed by chromatography (thermal-conductivity detector).

#### **RESULTS AND DISCUSSION**

#### Nanosize Effect in the Genesis of Aluminum–Manganese Catalysts

The preparation of supported catalysts from the supersaturated solutions of active metal salts under nonequilibrium conditions (method I) resulted in the dispersion of active components in porous support matrices; it provided an opportunity to avoid the precip-

itation of sparingly soluble metal salts on the catalyst surface and to shorten the impregnation time [3].

In accordance with the Gibbs theory of homogeneous nucleation [17], the crystallites formed in the course of crystallization from supersaturated solutions are smaller than those obtained using dilute solutions. However, these crystallites undergo rapid agglomeration on heating. It was found [18] that, in the presence of porous matrices, in which the resulting clusters are isolated from each other, an increase in the temperature did not cause the growth of particles. A limited concentration of a solute within a pore resulted in the formation of a cluster with a limiting volume  $n_{max}$  (where *n* is the number of atoms in the cluster); thereafter, the growth of clusters became energetically unfavorable. An analysis of changes in the Gibbs free energy function  $\Delta G = f(n)$ , which characterizes the growth of clusters with increasing n, for dilute and supersaturated solutions in an infinite volume and a closed pore demonstrated that a minimum value corresponds to the smallest cluster obtained from a supersaturated solution in a closed pore. Consequently, published data [17, 18] form the theoretical basis of the procedure proposed for preparing supported nanosized catalysts from supersaturated solutions.

Figure 1 shows the temperature dependence of methane conversion into  $CO_2$  on modified manganese catalysts supported onto A-1, ShN-2, and alumina prepared by the sol–gel method before and after treatment at 900°C (method I). For comparison, data on the conversion of methane on an analogous catalyst prepared by ordinary impregnation of the A-1 support with metal salts (method II) are given. As can be seen in Fig. 1, the initial catalysts can be arranged in the following order of increasing activity (depending on the nature of the support and the preparation procedure):

ShN-2 (method I) > A-1 (method I) > Al<sub>2</sub>O<sub>3</sub> (sol-gel; method I) > A-1 (method II).

For the most active sample supported on ShN-2,  $T_{10} = 400^{\circ}$ C and  $T_{80} = 500^{\circ}$ C, whereas the corresponding values for a sample based on Al<sub>2</sub>O<sub>3</sub> (sol–gel) are 400 and 550°C, respectively. Consequently, the temperature at which 80% methane conversion was reached on the catalyst prepared by method I is lower by 50°C than that on the catalyst synthesized using the ordinary impregnation method.

After the treatment of catalysts at 900°C for 5 h, the order of activity remained unchanged; however, the conversion of methane decreased by 10–15%, and the activity of a sample on the support synthesized by the sol–gel method decreased by 30%. Note that, even after calcination at 900°C, the activity of the aluminum–manganese catalyst prepared by method I was higher than the activity of an analogous sample prepared by ordinary impregnation and not subjected to high-temperature treatment. Thus, the activity and thermal stability of catalysts of the same chemical composition

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Sample	600°C, 2 h			900°C, 5 h			
Sample	$S_{\rm sp}, {\rm m^2/g}$	phase	$L(Al_2O_3)$ , nm	$S_{\rm sp},  {\rm m^2/g}$	phase*	$L(Al_2O_3)$ , nm	
A-1	193	γ	4	78	θ, (γ)	10	
ShN-2	116	χ	6	33	æ, ( <b>x</b> )	11	
Al <sub>2</sub> O <sub>3</sub> (sol-gel)	93	_	_	5	α	>20	
Mn-REE, AEE/A-1	184	γ	4	98	$\theta$ , $\gamma$ , Mn <sub>2</sub> O <sub>3</sub> , Mn <sub>3</sub> O <sub>4</sub>	6	
Mn-REE, AEE/ShN-2	68	χ	7	53	$\chi$ , Mn <sub>2</sub> O <sub>3</sub> , Mn <sub>3</sub> O <sub>4</sub>	9	
Mn–REE, AEE/Al <sub>2</sub> O <sub>3</sub> (sol–gel)	65	_	-	7	$\alpha$ , La <sub>2</sub> O <sub>3</sub> · 11Al <sub>2</sub> O <sub>3</sub>	>20	

 Table 1. Structure properties of aluminum oxides and aluminum-manganese catalysts (method I)

\* Trace amounts of other phases are given in parentheses.

Table 2. Pore-structure characteristics of aluminum oxides and catalysts based on them

Sample	Total pore volume, cm <sup>3</sup> /g	Micropore volume, cm <sup>3</sup> /g	Predominant pore diameter, nm
A-1	0.58	0.098	8.1
ShN-2	0.25	0.047	7.0-8.0
Al <sub>2</sub> O <sub>3</sub> (sol-gel)	0.02	-	-
Mn-REE, AEE/A-1 (600°C)	0.46	0.081	7.8
Mn-REE, AEE/A-1 (900°C)	0.28	0.052	15.1
Mn-REE, AEE/ShN-2 (600°C)	0.21	0.048	7.0
Mn-REE, AEE/ShN-2 (900°C)	0.17	0.030	9.8

can be enhanced by the optimization of the preparation procedure.

To find the reason for the higher activity of samples synthesized by method I, we studied the phase composition of catalysts and corresponding supports after treatment at 600°C (2 h) and 900°C (5 h) (Table 1). According to XRD data,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\chi$ -Al<sub>2</sub>O<sub>3</sub> are the main phases of A-1 and ShN-2 supports, respectively. The crystallite sizes (*L*), which were determined using the lines 2 $\theta$  = 45.74 and 67° for A-1 and 2 $\theta$  = 67.3° for ShN-2, were equal to 4 and 6 nm, respectively. Diffraction maximums were absent from the X-ray diffraction pattern of Al<sub>2</sub>O<sub>3</sub> (sol–gel); this fact suggests that the sample was amorphous [19].

A study of the pore structure of samples (Table 2) demonstrated that A-1 and ShN-2 supports are nanosized porous matrices with different total pore volumes. In the A-1 support, the total volume of pores 4–18 nm in diameter was 0.58 cm<sup>3</sup>/g with the predominance of pores 8.1 nm in diameter. In the ShN-2 support, the total volume of pores 4–18 nm in diameter was 0.25 cm<sup>3</sup>/g, and pores 7.5–8 nm in diameter were predominant. The sample of Al<sub>2</sub>O<sub>3</sub> (sol–gel) was a wide-pore material with a pore volume of 0.02 cm<sup>3</sup>/g and a globule size of 17–21.5 nm, which was calculated from the equation  $L = 6000/(S_{sp}\rho_{true})$  [17].

The X-ray diffraction pattern of a catalyst prepared based on A-1 was identical to the X-ray diffraction pattern of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with the same particle size (we failed to detect a manganese-containing oxide phase). The X-ray diffraction pattern of a catalyst based on ShN-2 exhibited diffuse low-intensity diffraction peaks due to a  $\chi$ -Al<sub>2</sub>O<sub>3</sub> phase with L = 7 nm; as in the case of the catalyst based on A-1, phases corresponding to supported oxides were not observed. Rare earth and alkaline earth oxides were not detected because their concentrations in the catalysts are lower than the detection limit of this technique. The X-ray amorphism of manganese oxides can be explained by their low crystallinity, which resulted from the synthesis temperature insufficiently high for the formation of a long-range order structure, or the small size of manganese oxide particles  $(L \leq 3 \text{ nm})$ . An unmodified manganese catalyst with a higher manganese oxide content (10% on a metal basis) synthesized under analogous conditions was studied to more accurately determine the phase composition and crystallite size of catalysts. It was found that a tetragonal modification of Mn<sub>3</sub>O<sub>4</sub> with Mn<sub>2</sub>O<sub>3</sub> impurities was the main phase of manganese oxides. The crystallite size of Mn<sub>3</sub>O<sub>4</sub> was 5–6 nm, as determined from the line  $2\theta = 45.667^{\circ}$ . These data suggest the formation of fine manganese oxide particles in modified catalysts with a lower manganese concentration (5 wt %).

It is likely that the blocking of pores with active components was responsible for the observed decrease in the specific surface areas of modified catalysts based on A-1 and ShN-2, as compared with those of pure supports (in both cases, the total pore volume decreased by 20%). A more dramatic decrease in the specific surface area of the catalyst supported on ShN-2 can be due to the fact that the total pore volume of this catalyst is lower than that of A-1 by a factor of 2. The specific surface area of the catalyst based on Al<sub>2</sub>O<sub>3</sub> (sol–gel) can decrease because of the solid-phase interaction of active components with the support [5].

After treatment at 900°C for 5 h, the X-ray diffraction patterns of the supports exhibited diffraction lines due to the following high-temperature modifications of aluminum oxide:  $\theta$ -Al<sub>2</sub>O<sub>3</sub> with a small impurity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for A-1, æ-Al<sub>2</sub>O<sub>3</sub> with an impurity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for ShN-2, and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> for the sample of Al<sub>2</sub>O<sub>3</sub> (sol-gel). The appearance of the above phases corresponds to the sequence of phase transformations in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $\chi$ -Al<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub> (sol-gel) in the course of high-temperature treatment [20], and it was accompanied by a noticeable decrease in the degree of dispersion. The crystallite size was estimated at ~10-11 nm (A-1 and ShN-2). In this case, the specific surface area decreased to 78 (A-1) or 33 m<sup>2</sup>/g (ShN-2). The sample of  $Al_2O_3$  (sol-gel) was characterized by a well-crystallized  $\alpha$  phase with a specific surface area of 5  $m^2/g$ .

A comparison between the X-ray diffraction patterns of the catalyst on ShN-2 before and after hightemperature treatment indicates that the composition of the support remained unchanged ( $\chi$ -Al<sub>2</sub>O<sub>3</sub>), but the crystallite size increased to 9 nm. In addition, diffraction peaks due to the manganese oxides  $Mn_2O_3$  and Mn<sub>3</sub>O<sub>4</sub> were detected. The weak and diffuse reflections of the above oxides are indicative of a small particle size  $(L \sim 3 \text{ nm})$ , which is smaller than the particle size of the support. The absence of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase from the diffraction pattern of the calcined catalyst suggests a stabilizing effect of La, Ba, and Sr additives, which inhibit the phase transformations of the support. In the catalyst based on A-1, the phase composition of the support somewhat changed (a  $\theta$  phase appeared); the size of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> crystallites increased to 6 nm; and, as in the study by Stohmeir and Hercules [21], diffraction peaks due to the manganese oxides  $Mn_2O_3$  and  $Mn_3O_4$ were detected. The stabilizing effect of additives consists in the inhibition of  $Al_2O_3$  phase transformations. It manifested itself in the fact that the specific surface area of catalysts after heating at 900°C (5 h) decreased much less than the  $S_{sp}$  of a pure support. The formation of  $\theta$ -Al<sub>2</sub>O<sub>3</sub> even in the presence of stabilizing additives can be explained by the phase size effect. According to Uvarov and Boldyrev [22], this effect consists in a decrease in the phase transformation temperatures of aluminum oxide with decreasing particle size.

The stabilizing effect of La, Ba, and Sr additives was not found in the catalyst on amorphous  $Al_2O_3$  (sol-gel). As in the case of the pure support, the specific surface area of the catalyst decreased by almost one order of magnitude (to 7 m<sup>2</sup>/g), and the X-ray diffraction pattern exhibited diffraction lines characteristic of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and the lanthanum aluminate La<sub>2</sub>O<sub>3</sub> · 11Al<sub>2</sub>O<sub>3</sub> [23], the crystallite size of which is greater than 20 nm. Thus, the Al<sub>2</sub>O<sub>3</sub> (sol-gel) support is more reactive than the A-1 and ShN-2 supports toward both solid-phase interactions with active catalyst components (La<sub>2</sub>O<sub>3</sub>) and intrinsic phase transformations. This fact can explain the lower activity and stability of catalysts based on this support.

The XRD analysis of alumina supports and manganese catalysts based on these supports with the modifying additives of rare earth and alkaline earth elements (before and after treatment at 900°C) suggests that the catalysts can be arranged in the following order with respect to thermal stability to phase transformations:

 $Mn-REE, AEE/\chi-Al_2O_3 \ge Mn-REE, AEE/\gamma-Al_2O_3 > Mn-REE, AEE/Al_2O_3 (sol-gel),$ 

which is consistent with the activity order of catalysts prepared using method I.

A number of samples were studied by TPR in order to evaluate the oxygen-catalyst bond strength; the initial rate of reduction of oxides with hydrogen (reducibility) can serve as a relative characteristic of this bond strength. Hydrogen consumption maximums are absent from the TPR curves of the A-1 and ShN-2 supports; this fact suggests a high strength of the M-O bond in aluminum oxides and, consequently, the absence of catalytic activity. The TPR curves of manganese catalysts based on ShN-2 and A-1 are characterized by a wide region of hydrogen consumption with a diffuse maximum at 370°C (Fig. 2). This result is consistent with data published by Kapteijn et al. [24], who attributed this maximum to the reduction of fine  $Mn_2O_3$  in the aluminum-manganese catalyst. According to Stohmeir and Hercules [21],  $Mn_2O_3$  with a particle size of 5–6 nm is the main manganese phase in the 4% Mn/Al<sub>2</sub>O<sub>3</sub> catalyst. The absence of diffraction maximums corresponding to manganese oxides can be explained by their smaller particle size, which resulted from the catalyst preparation procedure. The catalyst based on ShN-2 was characterized by a broader (170–650°C) and less intense region of hydrogen consumption, as compared with the sample based on A-1 (250–550°C). This result can be explained by the difference between the pore structures of the supports: the broader range of predominant pore diameters in ShN-2 (7-8 nm) can lead to an analogous size distribution of supported oxides. The diffuse maximum in the TPR curve of the catalyst based on ShN-2 suggests the appearance of an internal size effect in the aluminum-manganese nanosystem [25]: a decrease in the reduction temperature of manganese oxide to  $170^{\circ}$ C with decreasing particle size. After the treatment of catalysts at 900°C, the maximum intensity of hydrogen consumption dramatically decreased. As found by XRD, this was due to the conversion of Mn<sub>2</sub>O<sub>3</sub> into Mn<sub>3</sub>O<sub>4</sub>, which undergoes reduction at a higher temperature. A comparison of the TPR curves of manganese catalysts calcined at 900°C demonstrated that the TPR peak intensity of the sample based on ShN-2 was higher than that on A-1; this suggests the retention of a considerable amount of Mn<sub>2</sub>O<sub>3</sub> in the former sample. This can explain the higher activity of the sample based on ShN-2 after treatment at 900°C.

To study the effect of the nature of the transition metal on the activity of aluminum oxide catalysts, we synthesized (using method I) and tested samples based on A-1 modified with rare earth and alkaline earth elements. In these samples, the oxides of copper, chromium, and cobalt and their mixtures, in particular, with manganese oxide, were used as active components (Fig. 3). The experimental data suggest that the catalysts are arranged in the following order of activity in deep methane oxidation:

MnLaBaSr > MnCuLaBaSr > CuLaBaSr > CuCrLaBaSr > CoREEBaSr > CoLaBaSr > Co.

The MnLaBaSr catalyst was more active than the samples containing the oxides of other transition metals (Cu, Cr, and Co) or their binary compositions. Therefore, aluminum-manganese catalysts are promising for use in the test reaction and it is reasonable to optimize their composition further.

Thus, the study of the structure and texture characteristics of aluminum-manganese catalysts for deep methane oxidation demonstrated that the supporting of an active component and stabilizing additives (La, Ba, and Sr) under nonequilibrium conditions resulted in the formation of nanosized active phases in the porous matrix of an  $Al_2O_3$  support, the retention of nanosized alumina particles, and the stabilization of low-temperature alumina modifications ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\chi$ -Al<sub>2</sub>O<sub>3</sub>). This is responsible for the higher activity (100% methane conversion was reached at 550-600°C) and thermal stability of aluminum-manganese systems synthesized by the proposed procedure, as compared with the wellknown catalysts of analogous composition prepared using traditional impregnation [26, 27]. The appearance of an internal size effect in the aluminum-manganese nanosystem was found, which consisted in a decrease in the phase transformation temperatures of aluminum oxide and the reduction temperature of manganese oxide with decreasing particle size.

# Effect of the Size Factor on the Catalytic Properties of Spinel Ferrites

Along with highly dispersed aluminum oxide systems, the use of nanosized complex spinel oxide cata-

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Hydrogen consumption



**Fig. 2.** TPR curves of aluminum–manganese catalyst samples based on A-1 and ShN-2 after thermal treatments under various conditions: (*1*) Mn–REE, AEE/A-1 (900°C), (*2*) Mn–REE, AEE/A-1 (600°C), (*3*) Mn–REE, AEE/ShN-2 (900°C), and (*4*) Mn–REE, AEE/ShN-2 (600°C).



**Fig. 3.** The temperature dependence of methane conversion on modified oxide catalysts based on A-1: (*1*) Co, (2) CoREEBaSr, (3) CoLaBaSr, (4) CuLaBaSr, (5) CuCrLa-BaSr, (6) MnCuLaBaSr, and (7) MnLaBaSr.

lysts in the reaction of deep methane oxidation seems promising.

The most effective spinels are the ferrites  $MFe_2O_4$ (M = Mn, Co, Ni, and Zn), which exhibited higher activity in the test reaction than that of aluminates. They are less toxic and less expensive than chromites; their stability under oxidizing conditions is higher than that of cobaltites [28, 29].

Table 3 summarizes the structure characteristics (phase composition, crystallite size, and  $S_{sp}$ ) and catalytic activity (temperatures at which 10, 50, and 100% methane conversion was reached) of bulk ferrites.

Sample	Indexed phases	L (CSR), nm	$S_{\rm sp}^*$ , m <sup>2</sup> /g	Temperature* at which specified methane conversion was reached, °C		
	(inodification)		I	10%	50%	100%
CoFe <sub>2</sub> O <sub>4</sub>	CoFe <sub>2</sub> O <sub>4</sub>	9	47.0	<350	410	500
			0.6	550	**	**
NiFe <sub>2</sub> O <sub>4</sub>	NiFe <sub>2</sub> O <sub>4</sub>	8	35.0	375	460	550
			0.8	525	650	**
MnFe <sub>2</sub> O <sub>4</sub>	MnFe <sub>2</sub> O <sub>4</sub>	15	27.0	450	515	650
			0.4	600	**	**
CoFe <sub>2</sub> O <sub>4</sub>	CoFe <sub>2</sub> O <sub>4</sub>	>50	15.0	425	515	600
(from inorganic salts)			_	-	-	_
NiFe <sub>2</sub> O <sub>4</sub>	NiFe <sub>2</sub> O <sub>4</sub>	>50	16.0	410	480	600
(from inorganic salts)			_	-	-	_
$CoFe_2O_4$ + surfactant	CoFe <sub>2</sub> O <sub>4</sub>	7.5	54.0	<350	370	500
			5.0	500	650	**
$NiFe_2O_4$ + surfactant	NiFe <sub>2</sub> O <sub>4</sub>	8	33.0	375	450	550
			7.0	500	600	**

**Table 3.** Structure characteristics and catalytic activity of bulk ferrites

\* Top, initial catalyst; bottom, catalyst after heating at 900°C for 5 h.

\*\* The specified conversion was not reached on the sample over a temperature range to 650°C.

According to XRD data, all of the tested ferrite samples exhibited a cubic spinel structure and the particle size of these samples depended on preparation procedure. Spinels with a particle size from 7.5 to 15 nm were formed in ferrite synthesis by the thermal decomposition of polynuclear complexes, whereas analogous samples prepared by the decomposition of inorganic salts contained particles of size >50 nm. Modification with surfactant additives had no effect on the particle size of nickel ferrite and somewhat increased the degree of dispersion of cobalt ferrite.

Nanosized cobalt and nickel ferrites (L = 8-9 nm), which were synthesized from heterometallic trinuclear complexes, were much more active than analogous spinels prepared by coprecipitation from metal salt solutions (Table 3): the temperatures of 10 and 100% methane conversion on nickel and cobalt ferrites were lower by 50 and 100°C, respectively.

A comparison of the specific catalytic activity of spinels, which were prepared using various techniques, at relatively low temperatures (to 450°C) indicated the effect of the size factor on the reaction rate of deep methane oxidation. This effect consists in an increase in the specific catalytic activity of cobalt and nickel ferrites with decreasing particle size (the specific catalytic activity of spinels  $w \times 10^3$ , ml CH<sub>4</sub> m<sup>-2</sup> min<sup>-1</sup>, is given in parentheses):

 $NiFe_2O_4 (9.1) > CoFe_2O_4 + surfactant (8.0)$ >  $CoFe_2O_4 (6.3) > NiFe_2O_4 (from inorganic salts) (3.4)$ 

## > CoFe<sub>2</sub>O<sub>4</sub>(from inorganic salts) (0).

The best results were obtained for cobalt and nickel ferrites with a particle size of 7.5–9 nm. The retention of the particle size of catalysts in the nanometer range, which is optimal for the occurrence of the given reaction, is responsible for high catalytic activity in deep methane oxidation [2, 30].

All of the ferrites have the same structure of the inverse spinel [31]; therefore, it is most likely that difference in their catalytic activity depends on the properties of the  $M^{2+}$  cation, which is a constituent of spinel. The lower catalytic activity of manganese ferrite is related to its instability on heating under oxidizing conditions. According to XRD, thermal analysis, and IRspectroscopic data [31], the growth of particles and the decomposition of manganese-containing spinel into oxides (MnO, which was oxidized to  $Mn_2O_3$ ; Fe<sub>2</sub>O<sub>3</sub>) were observed on heating above 400°C; this was accompanied by the agglomeration of particles and a decrease in  $S_{sp}$  (Table 3). The heating of cobalt- and nickel-containing catalysts over the temperature range 400–700°C was not accompanied by the decomposition of spinels.

The higher activity of cobalt ferrite can be due to the fact that an oxygen environment in the lattice of a complex oxide facilitates the transition of a transition metal ion to the highest oxidation state ( $Co^{3+}$ ). Moreover, according to Tret'yakov [32], because of a relatively low energy of disordering, the surface layer of cobalt

Sample	Indexed phases (modification)	$S_{\rm sp}^*$ , m <sup>2</sup> /g	Temperature* at which specified methane conversion was reached, °C		
			10%	50%	100%
CoFe <sub>2</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	$\chi$ -Al <sub>2</sub> O <sub>3</sub> (cubic)	96.0	425	540	650
		63.0	475	560	650
NiFe <sub>2</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	"	91.0	375	485	600
		61.0	450	550	650
CoFe <sub>2</sub> O <sub>4</sub> -Al <sub>2</sub> O <sub>3</sub>	"	78.0	460	560	650
(mix)		14.0	550	625	>650
NiFe <sub>2</sub> O <sub>4</sub> -Al <sub>2</sub> O <sub>3</sub>	"	91.0	410	500	600
(mix)		18.0	540	590	>650
$Al_2O_3$ (ShN-2)	"	116.0		Incotivo	I
		33.0	33.0 Inactive		
CoFe <sub>2</sub> O <sub>4</sub> /ZrO <sub>2</sub> -Y	ZrO <sub>2</sub> (cubic, monoclinic [traces])	9.5	400	463	600
NiFe <sub>2</sub> O <sub>4</sub> /ZrO <sub>2</sub> -Y	ZrO <sub>2</sub> (cubic, monoclinic [traces])	13.0	390	470	550
	ZrO <sub>2</sub> (cubic, monoclinic [traces]), NiFe <sub>2</sub> O <sub>4</sub>	-	-	_	_
ZrO <sub>2</sub> –Y	ZrO <sub>2</sub> (cubic, monoclinic [traces])	33.0	570	650	>650

**Table 4.** Structure characteristics and catalytic activity of supports and catalysts

\* Top, initial catalyst; bottom, catalyst after heating at 900°C for 5 h.

ferrite can be rapidly rearranged with a retention of the bulk in a stable state. This provides a rapid supply of oxygen, which is required for the occurrence of the reaction in accordance with the mechanism of deep hydrocarbon oxidation, to the catalyst surface.

After high-temperature treatment, the activity of catalysts decreased as a result of the agglomeration of spinel particles and the decrease of  $S_{sp}$  (Table 3). The modification of catalysts by surfactant additives had no effect on the activity of nickel ferrite, whereas the temperature at which high methane conversions were reached on cobalt ferrite decreased by 40°C. In this case, the catalysts exhibited higher thermal stability than that of analogous unmodified samples. It is likely that, on the addition of surfactant additives at the stage of catalyst preparation, a nanoparticle is surrounded by a layer of bulky structures, whose geometric size is responsible for the appearance of a steric barrier, which prevents the contact and agglomeration of nanoparticles.

Table 4 summarizes the results of a study of the structure characteristics and activity of supports and supported ferrite catalysts. The decrease of  $S_{sp}$  in catalysts based on ShN-2, as compared with that of the support, can be due to the blocking of pores with spinel particles because the total pore volume also decreased by 20%. As demonstrated above, the ShN-2 support—a nanosized porous matrix with a predominant pore diameter of 7–8 nm—is a low-temperature modification of  $\chi$ -Al<sub>2</sub>O<sub>3</sub> (Tables 1, 2).

According to XRD data (Fig. 4), the main phase of zirconium dioxide modified with  $Y_2O_3$  is cubic  $ZrO_2$ with small impurities of a monoclinic modification (curve 9). The X-ray diffraction patterns of supported samples exhibited diffraction maximums corresponding to the cubic modifications of supports: zirconium dioxide with small impurities of a monoclinic modification and aluminum oxide ( $\chi$ -Al<sub>2</sub>O<sub>3</sub>); the reflections of NiFe<sub>2</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> phases were absent (curves 3, 4, 7). The X-ray diffraction pattern of a catalyst prepared by mechanically mixing a ferrite with  $ZrO_2$  (curve 8) is identical to the X-ray diffraction patterns of a supported catalyst (curve 7) and a support (curve 9). The X-ray diffraction pattern of a catalyst prepared by mechanically mixing  $Al_2O_3$  with nickel ferrite (curve 1) is analogous to the diffraction pattern of the pure support calcined at 400°C for 5 h (curve 2). The X-ray diffraction patterns of supported samples exhibited no diffraction peaks corresponding to nickel and cobalt ferrites, the X-ray amorphism of which can be explained by high dispersion ( $L \leq 3$  nm). Moreover, reflections corresponding to a cubic spinel phase, which is isomorphous to cubic  $ZrO_2$  and  $Al_2O_3$  phases, can be masked by more intense diffraction peaks of supports. An additional argument for the formation of spinels in a porous support matrix is that the diffraction patterns of supported catalysts exhibited no reflections characteristic of a rhombohedral Fe<sub>2</sub>O<sub>3</sub> phase, which is a spinel decomposition product.



**Fig. 4.** X-ray diffraction patterns of support samples and ferrite catalysts: (1) NiFe<sub>2</sub>O<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub>, (2) Al<sub>2</sub>O<sub>3</sub> (400°C; 5 h), (3) NiFe<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>, (4) CoFe<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>, (5) Al<sub>2</sub>O<sub>3</sub>, (6) NiFe<sub>2</sub>O<sub>4</sub>/ZrO<sub>2</sub> (900°C; 5 h), (7) NiFe<sub>2</sub>O<sub>4</sub>/ZrO<sub>2</sub>, (8) NiFe<sub>2</sub>O<sub>4</sub>-ZrO<sub>2</sub>, and (9) ZrO<sub>2</sub>.

The X-ray diffraction pattern of a nickel-containing catalyst supported on  $ZrO_2$ , which was treated at 900°C for 5 h, exhibited diffraction peaks due to a cubic zirconia modification with small impurities of a monoclinic modification and a shoulder at about  $2\theta = 35.7^{\circ}$  (Fig. 4,

Table 5. TPR study of ferrite catalyst samples

Sample	Reduction onset temperature	Peak temperatures, °C		
	$(T_{o}), ^{\circ}\mathrm{C}$	T <sub>max1</sub>	$T_{\rm max2}$	
CoFe <sub>2</sub> O <sub>4</sub>	295	555	_	
NiFe <sub>2</sub> O <sub>4</sub>	365	525-580	_	
CoFe <sub>2</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	285	450	_	
NiFe <sub>2</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	350	435	_	
CoFe <sub>2</sub> O <sub>4</sub> /ZrO <sub>2</sub>	285	465	610	
NiFe <sub>2</sub> O <sub>4</sub> /ZrO <sub>2</sub>	210	385	600	
ZrO <sub>2</sub>	570	630	_	



Fig. 5. TPR curves of ferrite catalyst samples: (1) NiFe<sub>2</sub>O<sub>4</sub>, (2) CoFe<sub>2</sub>O<sub>4</sub>, (3) Fe<sub>2</sub>O<sub>4</sub>/ZrO<sub>2</sub>, (4) CoFe<sub>2</sub>O<sub>4</sub>/ZrO<sub>2</sub>, (5) NiFe<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>, and (6) CoFe<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>.

curve 6), which can be attributed to a cubic NiFe<sub>2</sub>O<sub>4</sub> phase. It is likely that the appearance of this phase was related to the growth of spinel grains due to the agglomeration of nanoparticles. The absence of reflections corresponding to a Fe<sub>2</sub>O<sub>3</sub> phase suggests that the NiFe<sub>2</sub>O<sub>4</sub> spinel did not decompose in the course of the high-temperature treatment of the supported catalyst.

A comparison between supported catalysts based on ferrites showed that the samples prepared by the decomposition of polynuclear complexes in the pores of a support  $(\gamma - Al_2O_3)$  were more active and more stable than the samples prepared by mechanically mixing ferrites with the support. A porous support matrix is a structural restrictor in the course of spinel agglomeration at high temperatures, which facilitates the retention of the catalytic activity of samples after high-temperature treatment. The difference in the catalytic activity of supported ferrites can be explained by the fact that cobalt ferrite is less stable than nickel ferrite [31]: after treatment at 700°C, spinel began to decompose into iron and cobalt oxides; the latter can react with the support to form inactive CoAl<sub>2</sub>O<sub>4</sub> [33]. The use of zirconium dioxide as a support for ferrites allowed us to decrease the temperature of the onset of reaction (10% methane conversion) and the temperature at which high methane conversions were reached, as compared with samples based on  $Al_2O_3$ .

Table 5 and Fig. 5 summarize the results of a TPR study of the redox properties of ferrite catalysts. The TPR profile of a  $CoFe_2O_4$  sample is characterized by lower temperatures of the onset of reduction  $(T_0)$  and maximum  $H_2$  consumption ( $T_{max}^{H_2}$ ), as compared with that of NiFe<sub>2</sub>O<sub>4</sub>. This suggests a lower bond strength of oxygen in the cobalt-containing ferrite. The TPR curve of modified zirconium dioxide exhibited a maximum in the region 570–740°C with  $T_{\text{max}}^{\text{H}_2}$  at 630°C. A shift of the  $T_{\text{max}}^{\text{H}_2}$  peak to the lower temperature region suggests a higher lability and/or reactivity of lattice oxygen in modified zirconium dioxide than that in Al<sub>2</sub>O<sub>3</sub> (ShN-2), which was not reduced over the test temperature range (to 900°C). The supported catalysts exhibited a decrease in  $T_0$  and  $T_{max}^{H_2}$ , as compared with bulk spinel samples; this can be due to an increase in the degree of dispersion of the ferrites. The TPR profile of the  $CoFe_2O_4/Al_2O_3$  catalyst is characterized by a broader and less intense region of hydrogen consumption than that of NiFe<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>. This can be due to the formation of CoAl<sub>2</sub>O<sub>4</sub> in supported cobalt ferrite; because of this, the amount of weakly bound oxygen, which is required for the occurrence of the reaction, decreased.

The supported zirconium oxide catalysts exhibited an increase in the intensity of hydrogen consumption, as compared with aluminum oxide catalysts. This can be due to an increase in the mobility of lattice oxygen in modified  $ZrO_2$  upon doping with ferrites. Moreover, unlike  $ZrO_2$ ,  $Al_2O_3$  and  $MeFe_2O_4$  crystallize in a spineltype structure; therefore, the isomorphous solid solutions of  $MeFe_2O_4$  with  $Al_2O_3$  can be formed along with ferrites. This increases the degree of interaction between ferrite and the support and, consequently, decreases the amount of weakly bound oxygen in catalysts supported on  $Al_2O_3$ , as compared with those on  $ZrO_2$ . The TPR data demonstrated that the amount and lability (reactivity) of oxygen increase in the order

$$CoFe_2O_4 > NiFe_2O_4 > NiFe_2O_4/ZrO_2$$
  
> CoFe\_2O\_4/ZrO\_2 > NiFe\_2O\_4/Al\_2O\_3  
> CoFe\_2O\_4/Al\_2O\_3 > ZrO\_2 > Al\_2O\_3.

This order is consistent with the order of activity of the test supports and catalysts that were not subjected to high-temperature treatment.

The activation of a C–H bond is required for the heterogeneous catalytic oxidation of hydrocarbons; the mechanism of this activation is under discussion [34– 38]. The activation of alkanes is related to the occurrence of atomic oxygen and acid–base sites on the catalyst surface [34]. Burch et al. [35] noted that the acti-

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vation of a C-H bond on the surface of an oxide catalyst can involve both homolytic and heterolytic decomposition. Because the C-H bond in methane is weakly acidic ( $pK_{\alpha} = 46$ ), the active surface sites capable of deprotonating CH<sub>4</sub> should be strongly basic. However, these sites rapidly undergo self-poisoning because of strong CO<sub>2</sub> adsorption. The acid-base pair of a metal cation (acid site) and an oxygen anion (basic site) is considered an active center for the deprotonation of the methane C-H bond on the surface of metal oxides. Deprotonation can result in the formation of adsorbed OH groups and the  $CH_3^-$  ion at the metal cation [36]. According to Wu et al. [37], the ignition temperature of deep propane oxidation decreased because of an increase in the acid site strength of catalysts based on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>. Yan et al. [38] believed that the protons of a support in cobalt-containing catalysts served as methane activation sites in the SCR process  $(CH_4 + NO + O_2 \longrightarrow N_2 + CO_2 + H_2O)$ . A study of the acid properties of supported ferrites using TPAD demonstrated that the surface concentration of acid sites in a sample based on Al<sub>2</sub>O<sub>3</sub>  $(3.1 \times 10^{-3} \text{ (mmol NH<sub>3</sub>)/m}^2)$ was higher than that in a sample based on  $ZrO_2$  (1.8 ×  $10^{-3}$  (mmol NH<sub>3</sub>)/m<sup>2</sup>). In this case, nickel ferrite supported on zirconium dioxide was characterized by the presence of stronger acid sites: the temperature of a desorption maximum of NH<sub>3</sub>  $(T_{\text{max}}^{\text{NH}_3})$  was equal to 300°C (against  $T_{\text{max}}^{\text{NH}_3} = 160^{\circ}\text{C}$  for NiFe<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>). The higher activity of NiFe<sub>2</sub>O<sub>4</sub>/ZrO<sub>2</sub> can also be related to the occurrence of stronger surface acid sites, which are of importance for deep hydrocarbon oxidation [37]. Consequently, a relationship between the activity and the redox and acid properties of supported ferrite catalysts was established.

Thus, as a result of the study of the spinel catalysts, we found that the ferrite preparation procedure affected the catalyst activity: the most active catalysts were nanosized cobalt and nickel ferrites prepared by the thermolysis of polynuclear iron complexes. In the presence of the CoFe<sub>2</sub>O<sub>4</sub> catalyst, the temperature of 100% CH<sub>4</sub> conversion was 500°C, which is lower than that on well-known spinel-type catalysts by 100–150°C [39–41]. It was found that the use of a support (Al<sub>2</sub>O<sub>3</sub>) and the addition of surfactants increased the thermal stability of catalysts. The effect of the size factor on the reaction rate of deep methane oxidation at relatively low temperatures (to 450°C) was found. This effect consists in an increase in the specific catalytic activity of cobalt and nickel ferrites with decreasing ferrite particle size.

# Effect of the Structure–Size Factor on the Catalytic Properties of Cobalt–Zirconium Nanosystems

The use of compositions based on  $ZrO_2$ , which exhibit high thermomechanical properties, and zeolites, in which supported elements occur in cavities, seems

Sample	Indexed phases* (modification)		$S_{\rm sp},{\rm m^2/g}$	Temperature* at which specified methane conver- sion was reached, °C	
				10%	80%
$\overline{(\mathrm{Co}_x\mathrm{O}_y-\mathrm{ZrO}_2)}$	ZrO <sub>2</sub> (cubic)	12–13	141	325	397
	Co <sub>3</sub> O <sub>4</sub>	14	5	400	589
	ZrO <sub>2</sub> (cubic [60%], monoclinic [30%])	28-30	-	-	-
$\overline{\mathrm{Co}_{x}\mathrm{O}_{y}/\mathrm{Zr}\mathrm{O}_{2}}$	Co <sub>3</sub> O <sub>4</sub>	12	19	367	490
(reagent grade)	ZrO <sub>2</sub> (monoclinic)	30	8	370	500
$\overline{\mathrm{Co}_{x}\mathrm{O}_{y}/\mathrm{Zr}\mathrm{O}_{2}}$	ZrO <sub>2</sub> (tetragonal [75%], monoclinic [15%])	12	62	363	467
(sol-gel)			9.6	409	520
$\overline{\text{Co}_x\text{O}_y/(\text{ZrO}_2-\text{Y})}$	Co <sub>3</sub> O <sub>4</sub>	13	50	280	475
	ZrO <sub>2</sub> (cubic [80%], monoclinic [10%])	16–17	_	_	_
	Co <sub>3</sub> O <sub>4</sub>	18–20	28	370	480
	ZrO <sub>2</sub> (cubic [80%], monoclinic [10%])	16–17	-	-	-
$\overline{\text{Co}_x\text{O}_y/[\text{ZrO}_2(\text{sol}-$	Co <sub>3</sub> O <sub>4</sub>	15	78	350	483
gel)–HTsVN]	ZrO <sub>2</sub> (tetragonal), pentasil	_	50	440	605
HTsVN	pentasil	-	_	575	>650
$\overline{\text{ZrO}_2 \text{ (reagent grade)}}$	ZrO <sub>2</sub> (monoclinic)	26–28	11	470	623
ZrO <sub>2</sub> (sol-gel)	ZrO <sub>2</sub> (tetragonal [75%], monoclinic [15%])	10-12	80	450	592
(ZrO <sub>2</sub> -Y)	ZrO <sub>2</sub> (cubic [90%], monoclinic [10%])	15–16	58	400	563

Table 6. Structure characteristics and catalytic activity of supports and catalysts

\* Top, initial catalyst; bottom, catalyst after heating at 800°C for 1 h.

effective in order to decrease the temperature of catalytic methane oxidation [42].

Table 6 and Fig. 6 show data on the catalytic activity of the test supports and cobalt-containing catalysts based on them. The conversion of methane on the  $Co_{y}O_{y}/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is given for comparison. The samples based on zirconium dioxide exhibited the highest activity in the test reaction. This activity was independent of procedures used for the preparation of both the support and the catalyst. The lowest temperatures of 80 and 100% methane conversion were observed in a coprecipitated sample ( $Co_xO_y$ –ZrO<sub>2</sub>). A comparison of the activities of zirconium-containing catalysts showed that the introduction of a modifier additive  $(Y^{3+})$  and the use of a sol-gel method for preparing the support resulted in a decrease in both  $T_{0}$  (10% conversion of  $CH_4$ ) and temperatures at which high methane conversions were reached. The activity of samples decreased after high-temperature treatment because of the agglomeration of catalyst particles, which was accompanied by a decrease in the specific surface area. The catalyst based on ZrO<sub>2</sub> modified with yttrium exhibited the highest thermal stability. Evidently, the addition of  $Y_2O_3$  at the stage of support preparation facilitated the uniform distribution of the additive between highly dispersed  $ZrO_2$  particles and prevented their agglomeration.

Catalysts based on zeolite HTsVN did not exhibit high activity: the complete oxidation of methane occurred at a temperature higher than 650°C. The use of the [ZrO<sub>2</sub> (sol-gel)-HTsVN] binary system as a support for cobalt oxides increased the activity of the catalyst, as compared with that of a sample based on HTsVN, and decreased the temperature of the onset of reaction, as compared with that on the  $Co_x O_y/ZrO_2$ (sol-gel) catalyst. The activity of a catalyst on a binary support reached a maximum upon promotion with Rh and Pd: the temperatures of the onset of reaction and 80% conversion of methane were lower by 50-90°C than those on an unpromoted sample. According to the electronic theories of catalysts, the introduction of a donor noble metal impurity into the composition of an oxide catalyst facilitates the activation of hydrocarbons because of a greater (than that of oxides) tendency to electron-acceptor interactions with oxygen. Moreover, promoters prevent agglomeration and recrystallization





**Fig. 6.** The temperature dependence of methane conversion on cobalt–zirconium oxide catalysts (a) before and (b) after treatment at 800°C. Catalysts: (1) ( $Co_xO_y$ –ZrO<sub>2</sub>), (2)  $Co_xO_y$ /ZrO<sub>2</sub> (reagent grade), (3)  $Co_xO_y$ /ZrO<sub>2</sub> (sol–gel), (4)  $Co_xO_y$ /ZrO<sub>2</sub>–Y, (5)  $Co_xO_y$ /[ZrO<sub>2</sub> (sol–gel)–HTsVN], (6)  $Co_xO_y$ /Al<sub>2</sub>O<sub>3</sub>, and (7)  $Co_xO_y$ /HTsVN.

processes in a catalyst based on the binary zeolite-containing composition during high-temperature treatment to enhance its thermal stability. A catalyst supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> exhibited the lowest activity: the temperatures of the onset of reaction and 80% conversion of methane were higher by 250–300°C than those on samples based on ZrO<sub>2</sub> and its modified forms.

Depending on the preparation procedure and the nature of the support, the catalysts are arranged in the following order of activity:

 $Co_xO_y - ZrO_2 > Co_xO_y/(ZrO_2 - Y)$ >  $Co_xO_y/ZrO_2(sol-gel) > Co_xO_y/[ZrO_2(sol-gel) - TsVN]$ >  $Co_xO_y/ZrO_2(reagent grade) > Co_xO_y/HTsVN$ >  $Co_xO_y/Al_2O_3.$ 

This order is consistent with the order of activity of pure supports; that is, the supports have a determining effect on the catalytic properties of supported cobalt oxides rather than serve as inert materials.

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Fig. 7. Electron micrographs of the samples of (a)  $ZrO_2$  modified with  $Y_2O_3$  and (b) a catalyst based on it; magnification, 82000×.

To reveal reasons for different activities of cobaltcontaining catalysts, we studied the structure characteristics, redox properties, and acid properties of a number of samples.

Table 6 summarizes the structure characteristics of supports and the most active catalysts. An analysis of the X-ray diffraction pattern of  $ZrO_2$  (reagent grade) demonstrated the presence of only a single phase: a monoclinic modification of zirconium dioxide with a particle size of 26-28 nm. According to XRD data, a tetragonal modification with a particle size of 10-12 nm was predominant in the sample of  $ZrO_2$  (sol-gel); the main phase of  $ZrO_2$  modified with  $Y_2O_3$  was a cubic modification of zirconium dioxide (L = 15-16 nm) with small monoclinic impurities. The use of a sol-gel method for the preparation of zirconium dioxide and the introduction of a modifying additive of  $Y_2O_3$  had a significant effect on the support particle size: the degree of dispersion increased by 45-55%. The X-ray diffraction pattern of a catalyst supported on modified zirconium dioxide exhibited diffraction maximums corre-

Sample	Hydrogen TPR data: reduction onset and peak temperatures, °C					
	T <sub>o</sub>	T <sub>max1</sub>	$T_{\rm max2}$	T <sub>max3</sub>		
$\overline{(\mathrm{Co}_x\mathrm{O}_y-\mathrm{ZrO}_2)}$	123	282	698	_		
$Co_xO_y/ZrO_2$ (reagent grade)	297	376	429	501		
$Co_xO_y/ZrO_2$ (sol-gel)	252	312	387	588		
$Co_xO_y/(ZrO_2-Y)$	≈60	383	429	454; >800		
$Co_xO_y/Al_2O_3$	454	481	555	_		
ZrO <sub>2</sub> (reagent grade)	642	725	-	_		
ZrO <sub>2</sub> (sol-gel)	580	670	-	_		
$(ZrO_2 - Y)$	≈60	400–450	>750	_		

**Table 7.** TPR study of the redox properties of supports and catalysts

sponding to  $Co_3O_4$  phases (L = 13 nm) and a cubic modification of the support with a particle size of 16– 17 nm. Electron micrographs (Fig. 7) support the nanodispersion of  $Y_2O_3$ -modified zirconium dioxide and a catalyst based on it; an analysis of these micrographs suggests sufficiently developed surfaces of the support and the catalyst with a particle size of 6–25 nm. These data are consistent with XRD data and the values of  $S_{sp}$ .

An analysis of the diffraction pattern of a sample based on  $ZrO_2$  (reagent grade) exhibited the presence of a  $Co_3O_4$  phase (L = 12 nm) and a monoclinic modification of the support. In a precipitated sample of  $Co_{v}O_{v}$ -ZrO<sub>2</sub> and a catalyst based on ZrO<sub>2</sub> (sol-gel), peaks corresponding to only a support phase were detected, whereas we failed to detect a cobalt-containing oxide phase. It is likely that the X-ray amorphism of cobalt oxides is explained by their high degree of dispersion because a  $Co_3O_4$  phase was detected in samples based on modified and laboratory (reagent grade) zirconium dioxides, which were synthesized at the same temperature (350-400°C). Moreover, reflections due to a cubic phase of highly dispersed  $Co_3O_4$ , which is isomorphous to a cubic ZrO<sub>2</sub> phase, in the diffraction pattern of the  $Co_xO_y$ -ZrO<sub>2</sub> sample can be masked by zirconia diffraction maximums, which are more intense. Evidently, the high dispersion of the active component and zirconia in the  $Co_xO_y$ –ZrO<sub>2</sub> and  $Co_xO_y$ /ZrO<sub>2</sub> (sol– gel) catalysts is responsible for their higher activity than that of samples based on  $ZrO_2$  (reagent grade) and modified zirconium dioxide (Fig. 6).

In addition to peaks that correspond to a tetragonal modification of  $ZrO_2$  and pentasil, the diffraction pattern of the [ $ZrO_2$  (sol-gel)–HTsVN] catalyst exhibited a number of reflections that suggested the occurrence of a  $Co_3O_4$  phase (L = 15 nm).

The phase composition of the most active  $Co_xO_y$ -ZrO<sub>2</sub> and  $Co_xO_y/(ZrO_2-Y)$  samples was also studied after treatment at 800°C for 1 h. The X-ray diffraction pattern of the coprecipitated catalyst exhibited diffraction maximums that corresponded to the cubic and monoclinic modifications of zirconium dioxide. The appearance of the latter modification corresponds to the sequence of ZrO<sub>2</sub> phase transformations in the course of high-temperature treatment [43], and it was accompanied by a considerable decrease in dispersion. The diffraction pattern also exhibited reflections due to a  $Co_3O_4$  phase; it is likely that the appearance of this phase was associated with a decrease in the degree of dispersion of cobalt oxide because of nanoparticle agglomeration.

Note that high-temperature heating caused a more dramatic decrease in  $S_{sp}$  and a decrease in the activity of  $Co_xO_y$ –ZrO<sub>2</sub> and  $Co_xO_y$ /ZrO<sub>2</sub> (sol–gel) samples, as compared with the catalyst based on ZrO<sub>2</sub> (reagent grade). This fact suggests the appearance of an internal size effect in a zirconium oxide nanosystem [22]: a decrease in the temperature of agglomeration with decreasing catalyst particle size. Moreover, the temperatures of phase formation and aggregation considerably decreased with the use of the sol–gel preparation method [5].

An increase in the treatment temperature of a catalyst based on modified  $ZrO_2$  resulted in the growth of active component particles. This manifested itself in the X-ray diffraction pattern as a decrease in diffraction peak widths; the degree of dispersion of the support remained unchanged. Thus, the modification of zirconia with yttrium oxide resulted in a deceleration of agglomeration processes and phase transformations; consequently, the specific surface area decreased to a lesser extent.

To determine the binding energy of surface oxygen, we studied catalyst samples using TPR (Table 7).

The TPR profiles of ZrO<sub>2</sub> (reagent grade) and ZrO<sub>2</sub> (sol-gel) exhibited weakly intense high-temperature hydrogen consumption regions. However, the ZrO<sub>2</sub> (sol-gel) exhibited a decrease in  $T_0$  and  $T_{\text{max}}^{\text{H}_2}$ , as compared with the corresponding values for ZrO<sub>2</sub> (reagent grade). The shifts of  $T_0$  and peak  $T_{\text{max}}^{\text{H}_2}$  to a lower temperature region indicate that the lability (reactivity) of lattice oxygen in ZrO<sub>2</sub> (sol-gel) is higher. The reduction of the ZrO<sub>2</sub>-Y support, which has a higher capacity for oxygen [13], occurred in two regions: a low-temperature region (60–640°C) with  $T_{\text{max1}}^{\text{H}_2}$  at 400–450°C and a high-temperature region (>672°C) with  $T_{\text{max2}}^{\text{H}_2} >$ 750°C. This suggests the occurrence of both relatively weakly bound and relatively strongly bound oxygen

weakly bound and relatively strongly bound oxygen species. The TPR data are consistent with the catalytic properties of the supports in methane oxidation with the labile oxygen of zirconium dioxide.

	$\rm NH_3$ desorption peak temperatures, °C		Acid site concentrations, (mmol NH <sub>3</sub> )/m <sup>2</sup>		
Sample	$T_{\rm max1}$	T <sub>max2</sub>	$K_1^{\text{NH}_3} \times 10^3,$ 170–250°C	$K_2^{\rm NH_3} \times 10^3,$ 250–450°C	$\Sigma K^{\rm NH_3} \times 10^3$
$(Co_xO_y-ZrO_2)$	200	280	0.28	0.45	0.73
$Co_xO_y/ZrO_2$ (reagent grade)	170	250	0.52	0.51	1.03
$Co_xO_y/ZrO_2$ (sol-gel)	180	270	0.72	0.98	1.7
$Co_xO_y/(ZrO_2-Y)$	250	395	0.28	0.12	0.4
Co <sub>x</sub> O <sub>y</sub> /HTsVN	210	450	3.8	2.8	6.6
$Co_xO_y/[ZrO_2(sol-gel)-HTsVN]$	200	450	1.6	1.0	2.6
$Co_xO_y/Al_2O_3$	180	_	_	-	2.2
ZrO <sub>2</sub> (reagent grade)	200	_	_	_	1.39
ZrO <sub>2</sub> (sol-gel)	210	_	_	-	2.8
$(ZrO_2 - Y)$	220	_	-	_	0.36

Table 8. TPAD study of the surface acid properties of supports and catalysts

In the presence of the active oxide component  $Co_3O_4$ , which can form nonstoichiometric phases with oxygen, the reducibility of catalysts increased, as compared with individual supports. This is reflected in a decrease of  $T_{\rm o}$  and  $T_{\rm max}^{\rm H_2}$  and in an increase in the intensity of hydrogen consumption in catalysts. The  $Co_v O_v$ - $ZrO_2$  and  $Co_xO_y/ZrO_2$  (sol-gel) samples exhibited a shift of  $T_0$  and  $T_{max}^{H_2}$  to the region of lower temperatures, as compared with the  $Co_r O_y / Zr O_2$  (reagent grade) sample. This can be due to the higher dispersion of both cobalt oxides and zirconium dioxide in these samples. It is likely that the presence of nonreducible zeolite as a constituent of the [ZrO<sub>2</sub> (sol-gel)-HTsVN] support was responsible for higher temperatures at which 80-100% conversion of methane was reached on the binary support, as compared with that for the sample based on  $ZrO_2$  (sol-gel). The TPR profile of the  $Co_rO_y/Al_2O_3$ sample was characterized by high values of  $T_{\rm o}$  and  $T_{\rm max}^{\rm H_2}$ 

sample was characterized by high values of  $T_0$  and  $T_{max}$ and a less intense region of hydrogen consumption than those for catalysts based on zirconium dioxide. This difference in reducibility can be explained by the fact that, unlike ZrO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> crystallize in a spinel-type structure, which is responsible for the formation of an isomorphous solid solution of Co<sub>3</sub>O<sub>4</sub> with Al<sub>2</sub>O<sub>3</sub> or spinel with CoAl<sub>2</sub>O<sub>4</sub>. This resulted in a decrease in the amount of weakly bound oxygen, which is necessary for the occurrence of a reaction. Thus, the results obtained using TPR demonstrated that the amount of labile oxygen increased in an order that is consistent with the order of activity of the test catalysts and individual supports.

An analysis of the surface acid properties of the test catalysts did not exhibit a simple correlation between

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activity and the concentration and strength of acid sites (Table 8). Nevertheless, the most active catalysts based on zirconium dioxide were characterized by the presence of stronger acid sites at an insignificant total concentration of acid sites. The introduction of zeolite into the composition of a ZrO<sub>2</sub> (sol–gel) support increased the strength and concentration of acid sites in the  $Co_xO_y/[ZrO_2 (sol–gel)–HTsVN]$  catalyst (Table 8, Fig. 8). It is likely that the presence of stronger acid sites on the surface of the  $Co_xO_y/[ZrO_2 (sol–gel)–HTsVN]$  catalyst was responsible for a decrease in the temperature of the onset of reaction on this sample, as compared with that on  $Co_xO_y/[ZrO_2 (sol–gel).$ 

Intensity



Fig. 8. Spectra of TPAD from the surface of cobalt catalysts supported on (1)  $ZrO_2$  (sol-gel) and (2) [ $ZrO_2$  (sol-gel)–HTsVN].

Thus, we found that the nature of the support and the procedures used for the preparation of both the support and the catalyst affected the activity of cobalt–zirconium nanosystems. We prepared low-temperature catalysts for deep methane oxidation under conditions developed for the formation of the nanosized phases of a support ( $L_{ZrO_2} = 12-13$  nm) and an active component ( $L_{Co_xO_y} \leq 3$  nm). In terms of activity, these catalysts are comparable with the well-known catalysts based on zirconium dioxide and with catalytic systems containing noble metals [44–46]. We found the manifestation of an internal size effect in the zirconium oxide nanosystem: a decrease in the temperature of agglomeration with decreasing catalyst particle size.

We found that the most active catalyst among supported ferrite and cobalt–zirconium nanosystems was characterized by the greatest amount and the highest reactivity of oxygen. The presence of strong acid sites on the catalyst surface was responsible for the lower temperature of the onset of the deep methane oxidation reaction. This is consistent with the current concepts of the mechanism of deep methane oxidation on oxide catalysts.

The results of the study of complex oxide nanocomposites in deep methane oxidation suggest that the problem of developing efficient catalysts that do not contain noble metals can be successfully solved based on the effect of structure-size (especially, nanosize) factors on the activity and thermal stability of catalysts and a relationship between the functional (redox and acid) and catalytic properties of the above oxide compositions. The nanosized supported zirconia- and alumina-based catalytic systems and spinel-structure  $MFe_2O_4$  nanocomposites (M = Mn, Co, or Ni) with controllable structure-size characteristics, redox properties, and acid properties form the basis for the development of commercial catalysts for the purification of methane-containing vent gas emissions and the combustion of hydrocarbon gas fuel in power plants.

#### ACKNOWLEDGMENTS

This study was performed within the framework of a project of the program "Nanostructured Systems, Nanomaterials, and Nanotechnologies" of the National Academy of Sciences of Ukraine.

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