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# $MnO_x$–$Al_2O_3$ Catalysts for Deep Oxidation Prepared with the Use of Mechanochemical Activation: The Effect of Synthesis Conditions on the Phase Composition and Catalytic Properties

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**Abstract**—The catalytic activity of alumina–manganese catalysts in the oxidation of CO was studied. The $MnO_x$–$Al_2O_3$ catalysts were prepared by an extrusion method with the introduction of mechanically activated components (manganese oxide and its mixtures with aluminum oxide, aluminum hydroxide, and a mixture of a manganese salt with aluminum hydroxide) into a paste of aluminum hydroxide followed by thermal treatment in air or argon at 1000°C. In the majority of cases, the catalysts contained a mixture of the phases of β-$Mn_3O_4$ ($Mn_2O_3$), α-$Al_2O_3$, and δ-$Al_2O_3$. The presence of low-temperature δ-$Al_2O_3$ suggested the incomplete interaction of manganese and aluminum oxides. It was found that the catalytic activity of $MnO_x$–$Al_2O_3$ depends on the degree of interaction of the initial reactants, and its value is correlated with the amount of β-$Mn_3O_4$ in the active constituent. The intermediate thermal treatment of components at 700°C negatively affects the catalytic activity as a result of the formation of $Mn_2O_3$ and the coarsening of particles, which levels the results of mechanochemical activation. The greatest degree of interaction between Al- and Mn-containing components was reached in the selection of mechanochemical activation conditions by decreasing the size of grinding bodies, optimizing the time of mechanochemical activation, and using the mechanochemical activation of precursor mixtures. As a result of mechanochemical activation, the initial reactants were dispersed, the amounts of $MnO_2$ and $Mn_2O_3$ changed, and defects were formed; this strengthened the interaction of components and increased catalytic activity.

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The alumina–manganese systems are active and thermostable catalysts of the deep oxidation of hydrocarbons and CO. Tsyrul'nikov et al. [1] discovered and studied in detail the effect of thermal activation—a significant increase in the catalytic activity of the 6–10 mol % $MnO_x$–$Al_2O_3$ system in the oxidation reactions of CO, butane, benzene, and cumene after the heat treatment of the samples at 900–1000°C. Based on the discovered effect, industrial catalysts [2–4] were developed for the removal of organic impurities and CO from gas emissions. These catalysts are thermostable up to 1000°C and resistant to the presence of chlorine-containing compounds and sulfur dioxide in waste gases at elevated temperatures. As found in further studies [5, 6], the thermal activation effect, which manifested itself after the heat treatment of $MnO_x$–$Al_2O_3$ at 900–1000°C, was due to the formation of the cubic spinel $Mn_{3-x}Al_xO_4$ ($x \approx 1.5$); on cooling, this spinel added oxygen and divided into layers with the separation of β-$Mn_3O_4$ oxide nanoparticles. It is important to ensure complete interaction between the initial reactants at the initial stages, which will facilitate the formation of $Mn_{3-x}Al_xO_4$ with an optimum composition in a maximum quantity upon the subsequent high-temperature treatment.

As is well known [7, 8], mechanochemical activation is a method for the preparation of fine-particle materials. In the joint mechanochemical activation of solid mixtures, the crushing and plastic deformation of substances are accompanied by an increase in the number of contacts between the particles and the appearance and migration of defects in the bulk of solids; this makes it possible to mix substances at the molecular level. Because of this, in some cases, catalysts obtained with the use of mechanochemical activation are similar to catalysts prepared by precipitation in terms of specific surface area and catalytic activity. From the industrial point of view, mechanochemical activation is a wasteless method unlike the traditional methods of catalysts preparation [9].

Mechanochemical activation can be used for both synthesizing supports and catalysts and imparting required performance properties (activity, strength, etc.) to them [7, 10]. Isupova et al. [11] found that the mechanochemical activation of manganese oxides for several minutes leads to an increase in the specific catalytic activity in the oxidation of CO by a factor of 2–5 depending on the chemical composition of the oxide; they explained this phenomenon by the appearance and accumulation of extensive defects along with dispersion.

The aim of this work was to study the influence of mechanochemical activation parameters on the interaction of manganese- and aluminum-containing reactants on the catalytic properties and phase composition of $MnO_x$–$Al_2O_3$ samples in order to determine the possibility of increasing their activity in the reaction of CO oxidation without changes in their empirical formulas. For selecting optimum precursors, the following mechanically activated substances and mixtures were investigated: $MnO_x$, $MnO_x + Al_2O_3$, $MnO_x$ + AlOOH, and $MnCO_3 \cdot Mn(OH)_2 \cdot nH_2O$ + AlOOH.

## EXPERIMENTAL

### Synthesis of Catalyst Samples

Mechanochemical activation was performed in an AGO-2S planetary activator mill (NPO Tekhnokom, Russia) on changing the $m_{\text{balls}}/m_{\text{sample}}$ ratio, the duration of mechanochemical activation, the diameter of grinding balls, and the rate of drum rotation (acceleration).

The catalyst samples (12 wt % $MnO_2$–$Al_2O_3$) were prepared by an extrusion method, in which manganese oxide powder or a mixture of manganese and aluminum oxides after mechanochemical treatment was introduced into a paste of aluminum hydroxide AlOOH, which contained a specified quantity of $HNO_3$ for peptization. The resulting mixture was dried to a plastic state, formed as extrudates with a diameter of 2 mm, dried at 120°C, and calcined at 950°C for 4 h.

### Physicochemical Characterization of Catalysts and Their Precursors

Physicochemical characteristics were studied by X-ray diffraction (XRD) analysis on a D8 diffractometer (Bruker, Germany) with the use of Cu$K_\alpha$ radiation with a wavelength of 1.5418 Å. The phase composition of the samples was established, the quantitative analysis of the samples was performed, and the average sizes of coherent scattering regions (CSRs) was determined.

Specific surface areas were measured on a Sorpty-1750 instrument (Carlo Erba, Italy) using the BET method based on the single-point adsorption of nitrogen at a pressure of 135 Torr and a temperature of 77 K with a relative error of ±4%.

### Catalytic Tests of the Samples in CO Oxidation

The catalytic experiments were carried out at 275°C in a flow glass reactor with dimensions of 170 mm × Ø 10 mm. The initial gas mixture consisted of 1% CO, 2% $O_2$, 8% $N_2$, and 89% He. To ensure measurements in the kinetically controlled region, a sample fraction of 0.8–1.4 mm was exposed to the reaction mixture at a reaction temperature for 1 h. In the course of the experiments, the flow rate of the gas mixture through the reactor was changed in a range of 200–570 mL/min for varying the residence time. The CO conversion on each of the samples was determined at four values of the residence time ($\tau$).

The reaction mixtures at the reactor inlet and outlet were analyzed on an LKkM-8MD chromatograph (Khromatograf, Soviet Union) on a column 3 m in length packed with zeolite CaA. The amount of unreacted CO was determined with the aid of a thermal conductivity detector.

The CO conversion was calculated from the equation

$$X(\mathrm{CO}) = (C_0 - C_{\text{out}})/C_0 = (S_{\text{in}} - S_{\text{out}})/S_{\text{out}},$$

where $S_{\text{in}}$ and $S_{\text{out}}$ are chromatographic peak areas corresponding to CO concentrations in the initial reaction mixture and at the reactor outlet, respectively; $C_0$ and $C_{\text{out}}$ are the initial CO concentration (1 vol %) in the mixture and the CO concentration at the reactor outlet (in vol %), respectively.

In the $X$(CO) range of 16–93%, the linear function $-\ln(1 - X) = f(\tau)$ was observed, which confirms a positive first order with respect to CO. Therefore, the rate constant of a first-order reaction with respect to CO was used as a characteristic of the catalytic activity in accordance with the equation

$$k = -\ln(1 - X)/\tau,$$

where $k$ is the reaction rate constant $s^{-1}$), $X$ is the CO conversion, and $\tau$ is the residence time (s).

The residence time $\tau$ was determined from the equation

$$\tau = m_{\text{Cat}}/V_{\text{gas}},$$

where $m_{\text{Cat}}$ is the catalyst volume ($cm^3$), and $V_{\text{gas}}$ is the feed flow rate ($cm^3$/s).

## RESULTS AND DISCUSSION

### Mechanochemical Activation of Manganese Oxide

To optimize catalysts preparation conditions with the use of a stage of the mechanochemical activation of manganese oxide, we studied the effect of mechanochemical activation parameters on the phase compositions and the particle sizes of the precursor and the catalyst.

**Table 1.** Structural parameters and catalytic activity of samples from series 1

| Sample | Acceleration, $g$ | $d_{ball}$, mm | Mechanochemical activation time, min | Precursor | | | Catalyst | |
|---|---|---|---|---|---|---|---|---|
| | | | | $Mn_2O_3$, % | CSR, Å | | $I(113)_{\alpha\text{-}Al_2O_3}/I(400)_{\delta\text{-}Al_2O_3}$ | $k$, $s^{-1}$ |
| | | | | | $MnO_2$ | $Mn_2O_3$ | | |
| 1.1 | – | – | – | 20 | 130 | >1000 | 0.5 | 3.3 |
| 1.2 | 30 | 8.5 | 5 | 24 | 120 | 170 | 1.0 | 2.7 |
| 1.3 | 30 | 8.5 | 10 | 30 | 130 | 150 | 1.4 | 2.8 |
| 1.4 | 30 | 8.5 | 20 | 50 | 130 | 130 | 2.7 | 2.9 |
| 1.5 | 30 | 8.5 | 30 | 76 | 160 | 160 | 1.5 | 1.8 |
| 1.6 | 30 | 7 | 30 | 20 | 110 | 120 | 1.9 | 3.8 |
| 1.7 | 100 | 7 | 10 | 100 | – | 200 | 1.4 | 1.4 |
| 1.8 | 30 | 5 | 30 | 14 | 100 | 130 | 2.3 | 4.4 |
| 1.9 | 30 | 5 | 10 | 14 | 100 | 200 | 3.8 | 4.4 |
| 1.10 | 30 | 5 | 20 | 20 | 100 | 200 | 3.7 | 5.4 |
| 1.11* | 30 | 5 | 10 | 14 | 100 | 200 | 4.2 | 5.3 |
| 1.12* | 30 | 5 | 20 | 20 | 100 | 200 | 5.8 | 6.0 |

$m_{manganese\ oxide}/m_{ball} = 1 : 40$.

* No intermediate heat treatment at 700°C.

**Effect of mechanochemical activation parameters on the properties of manganese oxide.** The initial manganese oxide contained 80 wt % $MnO_2$ and 20 wt % $Mn_2O_3$ with average CSR sizes of 130 and >1000 Å, respectively (Table 1). Mechanochemical activation led to a significant decrease in the CSR sizes of $Mn_2O_3$ from 1000 to 120–200 Å. Minimum particle sizes of manganese oxide (120 Å) were obtained at a grinding ball size of 7 mm, a mechanochemical activation time of 30 min, and a rotary acceleration of 30 $g$.

With the use of balls with a diameter of 8.5 mm, a change in the duration of mechanochemical activation from 5 to 30 min (samples 1.2–1.5) led to a decrease in the relative $MnO_2$ content. This fact is indicative of the conversion of $MnO_2$ into $Mn_2O_3$ accompanied by a loss of oxygen, which occurs under normal conditions at temperatures of 530–580°C. Within 5 min, the average CSR sizes considerably decreased to 170 Å for a phase of $Mn_2O_3$. A further decrease in the average CSR sizes of $Mn_2O_3$ to 130 Å with the retention of the CSR values of $MnO_2$ at a level of 120–130 Å was observed in a mechanochemical activation time range of 5–20 min. An increase in the mechanochemical activation time to 30 min led to an increase in the CSR sizes to 160 Å for both phases. This was likely due to an excess mechanochemical activation time, which led to the partial recrystallization of manganese oxide particles. With the use of balls 5 mm in diameter, the influence of the mechanochemical activation time on a change in the $MnO_2$ content was insignificant (Table 1, samples 1.8–1.10; Fig. 1).

An increase in the rotary acceleration of the mill facilitated a decrease in the fraction of $MnO_2$. Thus, at an acceleration of 100 $g$, $MnO_2$ (sample 1.7) was completely converted into $Mn_2O_3$ after mechanochemical activation for 10 min.

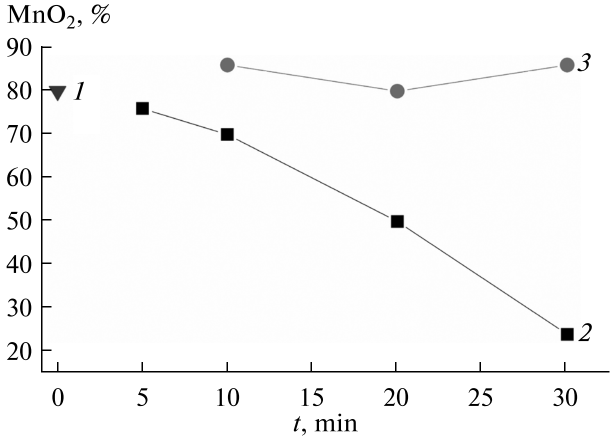

**Fig. 1.** Dependence of the relative $MnO_2$ content of the samples on the duration of mechanochemical activation at different sizes of grinding balls: (*1*) nonactivated sample and (*2* and *3*) samples activated at ball sizes of spheres 8.5 and 5 mm, respectively.

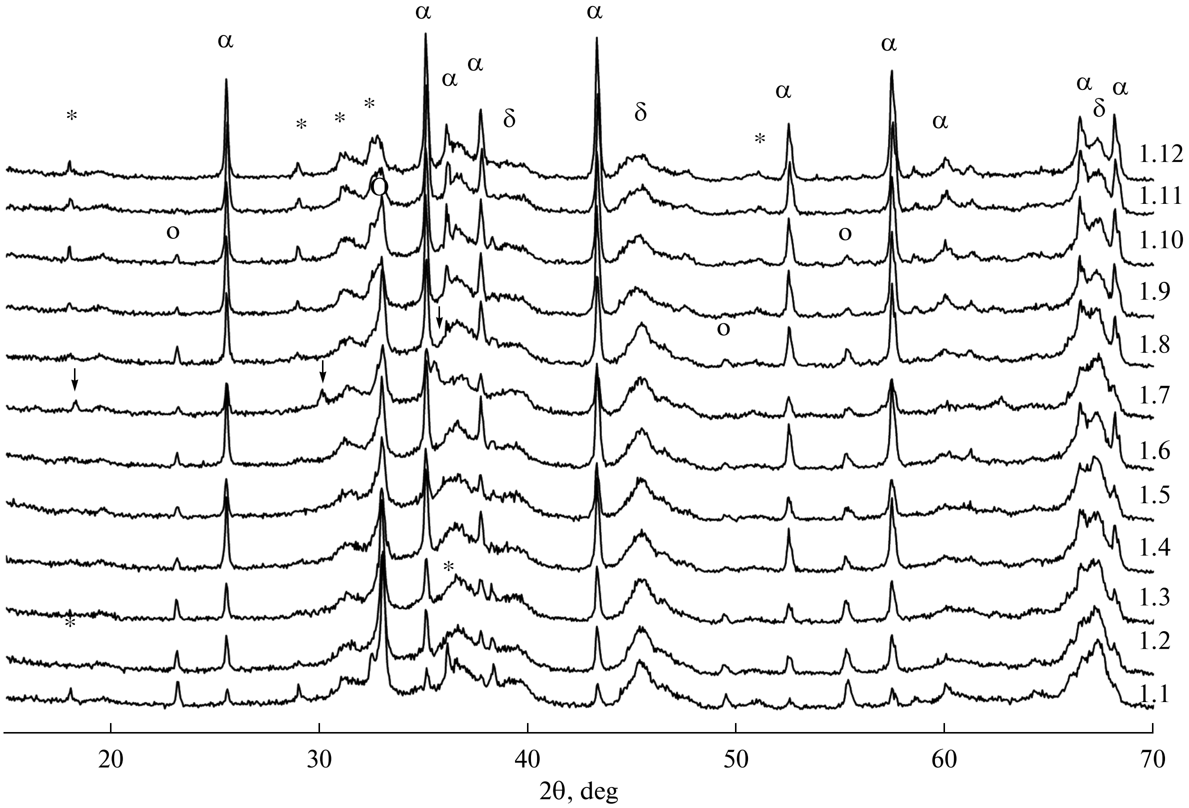

**Fig. 2.** X-ray diffraction patterns of the $MnO_x$–$Al_2O_3$ catalysts (series 1): ↓ – $Mn_2AlO_4$, * – $Mn_3O_4$ (tetragonal structure), α – α-$Al_2O_3$, o – $Mn_2O_3$ and δ – δ-$Al_2O_3$.

As follows from Fig. 1 and Table 1, as the diameter of balls was changed from 5 to 8.5 mm (30 *g*; 30 min; samples 1.8, 1.6, and 1.5), the concentration of the $MnO_2$ phase decreased from 86 to 24 wt %; in this case, the CSR sizes of $MnO_2$ increased from 100 to 160 Å. Consequently, as the size of grinding balls in the process of mechanochemical activation was increased, the occurrence of the reaction $4MnO_2 = 2Mn_2O_3 + O_2$ was accelerated and larger particles were formed.

Thus, the particles were dispersed in all mechanochemical activation regimes; however, under some conditions, the fraction of $Mn_2O_3$ sharply increased (up to 100%) and the same particle sizes could be reached without a change in the relative concentration of oxides under other conditions.

After the activation of manganese oxides, the catalysts were synthesized in accordance with the procedure described above (the activated component was introduced into a paste of aluminum hydroxide, which was extruded and calcined first at 700°C for 4 h and then at 950°C for 4 h).

**Phase composition and catalytic activity of catalysts prepared using activated manganese oxide.** The X-ray diffraction patterns of the majority of catalysts exhibited peaks corresponding to the phases of α-$Al_2O_3$, δ-$Al_2O_3$, β-$Mn_3O_4$, and $Mn_2O_3$ (Fig. 2). The $Mn_2AlO_4$ spinel was formed in sample 1.7 instead of β-$Mn_3O_4$, and the $Mn_2O_3$ oxide was not detected in samples 1.11 and 1.12. From Fig. 2, it follows that the peak intensity ratios of corundum (α-$Al_2O_3$) and δ-$Al_2O_3$ were different. Table 1 summarizes the structural parameters and phase compositions of the catalysts of series 1.

Large particles of β-$Mn_3O_4$ with CSR > 1000 Å were detected in sample 1.1, which was prepared with the use of the initial nonactivated manganese oxide; this was likely due to the presence of large $Mn_2O_3$ particles in the precursor. However, the catalysts obtained from the mechanically activated manganese oxides consisted of the fine particles of β-$Mn_3O_4$ with sizes of 30–50 Å. It should also be noted that the majority of samples contained $Mn_2O_3$ and δ-$Al_2O_3$ phases, which suggest the incomplete interaction of manganese and aluminum oxides.

According to published data [12], on the heat treatment of catalysts at 950°C, the initial reactants interact with the formation of a mixed Mn–Al solid solution based on the structure of spinel. The diffusion of manganese ions into the metastable phase of aluminum oxide facilitates the decomposition of the resulting nonequilibrium solid solution into $Al_2O_3$ and fine particles of β-$Mn_3O_4$:

$$MnO_x + \delta\text{-}Al_2O_3 \rightarrow Mn_xAl_yO_4$$
$$\rightarrow \alpha\text{-}Al_2O_3 + \beta\text{-}Mn_3O_4^*,$$

where β-$Mn_3O_4^*$ is the oxide containing Al atoms.

If this process occurred incompletely, the unreacted forms of low-temperature aluminum oxides remained in the catalyst. Based on X-ray diffraction data, it is difficult to calculate the concentration of the active phase $\beta$-$Mn_3O_4^*$ (because of the broadening of low-intensity peaks and overlapping with the reflections of other phases), but it is possible to estimate relative changes in the concentrations of $\alpha$-$Al_2O_3$ and $\delta$-$Al_2O_3$. From the reaction equation, it follows that the amount of the active phase $\beta$-$Mn_3O_4^*$ in the catalyst is directly proportional to the concentration of $\alpha$-$Al_2O_3$. Consequently, a coefficient equal to a ratio between the intensities of reflections 113 (corundum) and 400 ($\delta$-$Al_2O_3$), a transitional form of aluminum oxide, can be used as a tentative measure of the amount of $\beta$-$Mn_3O_4^*$ in the catalyst (or the degree of interaction between the parent substances).

According to the data of Table 1, the lowest degree of interaction was characteristic of sample 1.1, which was prepared from nonactivated manganese oxide, and the greatest degree was characteristic of samples 1.4, 1.6, and 1.8. Catalysts with the greatest degree of interaction were prepared from the mechanically activated precursors with the minimum sizes of the CSRs of $MnO_2$ (100–130 Å).

The low activity of catalyst 1.7 (prepared from the mechanically activated manganese oxide at an acceleration of 100 *g*), which contained the $Mn_2AlO_4$ spinel in place of $\beta$-$Mn_3O_4$ (as in the samples obtained at 30 *g*). It is believed that an increase in the catalytic activity of $MnO_x$–$Al_2O_3$ is due to the predominant presence of the $\beta$-$Mn_3O_4$ phase in the catalyst.

Let us consider in more detail the influence of mechanochemical activation conditions on the activity. A decrease in the size of grinding balls from 8.5 to 5 mm, all of the other parameters being the same (Table 1, samples 1.5, 1.8, 1.9), led to the strengthening of catalytic activity. The activity increased as the duration of mechanochemical activation was increased to 20 min, whereas a further increase the time of mechanochemical activation treatment to 30 min decreased the catalytic activity (Table 1, samples 1.2–1.5, 1.9, 1.10, 1.8).

The sequence of heat treatments influenced the catalytic activity. Samples 1.11 and 1.12, which were prepared without intermediate calcination at 700°C, had the highest characteristics of the degree of interaction and catalytic activity (Table 1). Unlike the other samples from the first series, the $Mn_2O_3$ manganese oxide was absent from these samples. Indeed, the $Mn_2O_3$ oxide is a thermodynamically equilibrium state at 700°C [13]; that is, intermediate heat treatment can decrease the effect of mechanochemical activation to cause the formation of $Mn_2O_3$ and the healing of defects, which will subsequently complicate interaction with aluminum oxide.

It is believed that the following factors affect the catalytic activity of the $MnO_x$–$Al_2O_3$ samples prepared from the activated manganese oxide: the decrease of the amount of $Mn_2O_3$ in the catalyst, the presence of the $\beta$-$Mn_3O_4$ phase, the high degree of interaction, and the predominant presence of the $MnO_2$ phase in the precursor after mechanochemical activation treatment.

Because the majority of samples contained the low-temperature phases of aluminum oxide and the $Mn_2O_3$ oxide (indicating the incomplete interaction of the reactants), we modified the preparation method: we excluded the stage of intermediate heat treatment at 700°C and used the simultaneous activation of manganese- and aluminum-containing reactants with the subsequent introduction of a mechanochemically activated component into aluminum hydroxide in order to improve the interaction of the components.

### *Simultaneous Mechanochemical Activation of Manganese and Aluminum Compounds*

We prepared three series of catalysts with the use of simultaneous mechanochemical activation. We used the following compositions of mechanochemically activated components: $MnO_x + Al_2O_3$ (series 2), $MnO_x$ + AlOOH (series 3), and $Mn(CO_3) \cdot nMn(OH)_2 \cdot mH_2O$ + AlOOH (series 4). The conditions of mechanochemical activation were optimized for each series. The Mn : Al ratio in the mechanochemically activated component was varied; however, in general, a constant chemical composition was maintained in the catalysts. The specific surface areas of the samples of different series were similar (31–41 $m^2/g$).

According to XRD data, the phases of $\alpha$-$Al_2O_3$, $\delta$-$Al_2O_3$, and $\beta$-$Mn_3O_4$ were present in the catalysts. Unlike series 1, the $Mn_2O_3$ oxide phase was not detected in series 2–4; this was likely due to a change in the preparation method because of the exclusion of the stage of intermediate calcination at 700°C.

As evidenced by data in Tables 2–4, the components interacted more completely as a result of the simultaneous activation. As in the case of samples 1.11 and 1.12, the simultaneous activation led to an increase in the catalytic activity. The degree of interaction and, correspondingly, the activity can be increased, as compared with those of the nonactivated sample, by a factor of more than 4 by varying the composition of the mechanically activated component.

An increase in the degree of interaction correlated with an increase in the catalytic activity. Figure 3 shows the reaction rate constant of CO oxidation on all of the samples as a function of the degree of interaction. At the degrees of interaction in a range from 0.5 to 5, the rate constant varied over a range of 1.5–6 $s^{-1}$; at these coefficients of 5–12, the rate constant increased to 13 $s^{-1}$ and then reached a plateau. In the

**Table 2.** Structural parameters and catalytic activity of samples from series 2

| Sample | $m_{Al_2O_3}/m_{MnO_x}$ | $m_{Cat}/m_{ball}$ | $d_{ball}$, mm | Mechanochemical activation time, min | Precursor | Catalyst | |
|---|---|---|---|---|---|---|---|
| | | | | | $Mn_2O_3$*, wt % | $I(113)_{\alpha\text{-}Al_2O_3}/I(400)_{\delta\text{-}Al_2O_3}$ | $k$, $s^{-1}$ |
| 2.1 | 1 : 1 | 1 : 40 | 7 | 20 | 20 | 5.6 | 5.0 |
| 2.2 | 1 : 1 | 1 : 67 | 7 | 20 | 28 | 4.4 | 3.1 |
| 2.3 | 1 : 1 | 1 : 40 | 5 | 20 | 18 | 5.0 | 6.4 |
| 2.4 | 1 : 1 | 1 : 67 | 5 | 20 | 18 | 5.8 | 7.4 |
| 2.5 | 1 : 1 | 1 : 40 | 3 | 20 | 20 | 5.8 | 6.5 |
| 2.6 | 1 : 1 | 1 : 67 | 3 | 20 | 24 | 9.2 | 10.0 |
| 2.7 | 1 : 1 | 1 : 67 | 3 | 10 | 22 | 5.6 | 7.4 |
| 2.8 | 1 : 1 | 1 : 67 | 3 | 30 | 0 | 12.0 | 11.2 |
| 2.9 | 1 : 2 | 1 : 40 | 5 | 20 | 22 | 5.3 | 3.5 |
| 2.10 | 2 : 1 | 1 : 40 | 5 | 20 | 14 | 16.6 | 9.2 |

The rotary acceleration of a drum on mechanochemical activation was 30 *g* for all of the samples from series 2 and 3.
* The weight fraction of $Mn_2O_3$ relative to manganese oxide contained in the mechanochemically activated catalyst precursor.

**Table 3.** Structural parameters and catalytic activity of samples from series 3

| Sample | $m_{AlOOH}/m_{MnO_x}$ | $m_{Cat}/m_{ball}$ | $d_{ball}$, mm | Mechanochemical activation time, min | Precursor | Catalyst | |
|---|---|---|---|---|---|---|---|
| | | | | | $Mn_2O_3$*, wt % | $I(113)_{\alpha\text{-}Al_2O_3}/I(400)_{\delta\text{-}Al_2O_3}$ | $k$, $s^{-1}$ |
| 3.1 | 1 : 1 | 1 : 40 | 7 | 20 | 16 | 2.9 | 4.3 |
| 3.2 | 1 : 1 | 1 : 67 | 7 | 20 | 13 | 5.5 | 4.9 |
| 3.3 | 1 : 1 | 1 : 40 | 5 | 20 | 15 | 6.6 | 8.2 |
| 3.4 | 1 : 1 | 1 : 67 | 5 | 20 | 13 | 4.5 | 7.5 |
| 3.5 | 1 : 1 | 1 : 40 | 3 | 20 | 14 | 5.7 | 9.7 |
| 3.6 | 1 : 1 | 1 : 67 | 3 | 20 | 17 | 9.4 | 13.0 |
| 3.7 | 1 : 1 | 1 : 67 | 3 | 10 | 16 | 8.5 | 11.8 |
| 3.8 | 1 : 1 | 1 : 67 | 3 | 30 | 15 | 5.9 | 9.3 |
| 3.9 | 1 : 2 | 1 : 40 | 5 | 20 | 16 | 2.7 | 4.7 |
| 3.10 | 2 : 1 | 1 : 40 | 5 | 20 | 15 | 13.5 | 12.0 |
| 3.11 | 2 : 1 | 1 : 67 | 3 | 20 | – | 14.2 | 13.9 |

The rotary acceleration of a drum on mechanochemical activation was 30 *g* for all of the samples from series 2 and 3.
* The weight fraction of $Mn_2O_3$ relative to manganese oxide contained in the mechanochemically activated catalyst precursor.

**Table 4.** Structural parameters and catalytic activity of samples from series 4

| Sample | MHC/AlOOH, mol/mol | $m_{Cat}/m_{ball}$ | Acceleration, $g$ | $d_{ball}$, mm | Mechanochemical activation time, min | Catalyst | |
|---|---|---|---|---|---|---|---|
| | | | | | | $I(113)_{\alpha\text{-}Al_2O_3}/I(400)_{\delta\text{-}Al_2O_3}$ | $k$, $s^{-1}$ |
| 4.1 | 1 : 3 | 1 : 40 | 30 | 5 | 15 | 2.9 | 4.3 |
| 4.2 | 1 : 3 | 1 : 40 | 30 | 5 | 15 | 6.3 | 5.9 |
| 4.3 | 1 : 3 | 1 : 40 | 100 | 5 | 15 | 5.2 | 5.6 |
| 4.4 | 1 : 3 | 1 : 40 | 60 | 5 | 15 | 5.0 | 4.9 |
| 4.5 | 1 : 3 | 1 : 40 | 30 | 8.5 | 30 | 5.0 | 4.6 |
| 4.6 | 1 : 3 | 1 : 40 | 30 | 7 | 30 | 4.6 | 4.4 |
| 4.7 | 1 : 3 | 1 : 40 | 30 | 5 | 30 | 4.6 | 4.7 |
| 4.8 | 1 : 3 | 1 : 40 | 30 | 3 | 30 | 4.0 | 5.3 |
| 4.9 | 1 : 3 | 1 : 40 | 30 | 5 | 5 | 6.1 | 7.5 |
| 4.10 | 1 : 5 | 1 : 40 | 30 | 5 | 30 | 23.3 | 12.2 |
| 4.11 | 1 : 1 | 1 : 40 | 30 | 5 | 30 | 1.7 | 2.6 |
| 4.12 | 1 : 3 | 1 : 67 | 30 | 5 | 30 | 6.8 | 6.4 |
| 4.13 | 1 : 5 | 1 : 40 | 30 | 5 | 15 | 39.3 | 13.0 |
| 4.14 | 1 : 5 | 1 : 40 | 30 | 5 | 5 | 18.6 | 13.7 |
| 4.15 | 1 : 5 | 1 : 40 | 30 | 5 | 10 | 20.2 | 13.1 |
| 4.16 | 1 : 5 | 1 : 40 | 30 | 7 | 30 | 14.2 | 9.7 |
| 4.17 | 1 : 5 | 1 : 40 | 30 | 3 | 30 | 30.0 | 12.0 |

MHC refers to manganese hydroxycarbonate.

presence of the $Mn_2O_3$ phase in the catalysts (series 1), the degree of interaction and the catalytic activity decreased.

Let us consider in more detail the effects of some mechanochemical activation parameters on the catalytic properties of the sample.

**Size of grinding bodies.** Figure 4 shows the dependence of the catalytic activity of $MnO_x$–$Al_2O_3$ on the size of grinding balls. It is evident that the activity increased with decreasing the size of the grinding bodies in all of the series.

The decrease of the diameter of balls facilitates the more intense occurrence of the processes of crushing and the deformation and interaction of oxide particles; this leads to an increase in the catalytic activity of the $MnO_x$–$Al_2O_3$ system.

**Duration of mechanochemical activation.** Figure 5 shows the dependence of the catalytic activity on mechanochemical activation time for each of series 2–4, all of the other mechanochemical activation parameters being the same. At short mechanochemical activation times (to 10–20 min), both the degree of interaction and the catalytic activity considerably increased, whereas, on the contrary, a further increase in the duration of mechanochemical activation to 30 min decreased these characteristics. An excess activation time decreased the catalytic activity; it is likely that this was facilitated by the aggregation of the already ground particles.

**Ratio between manganese- and aluminum-containing reactants in the mechanochemically activated component.** Figure 6 shows the results of a study of the influence of a ratio between manganese- and aluminum-containing reactants in their simultaneous activation on the catalytic activity. The testing of the synthesized samples in the reaction of CO oxidation and the results of XRD analysis showed (Tables 3 and 4) both the degree of interaction and the catalytic activity

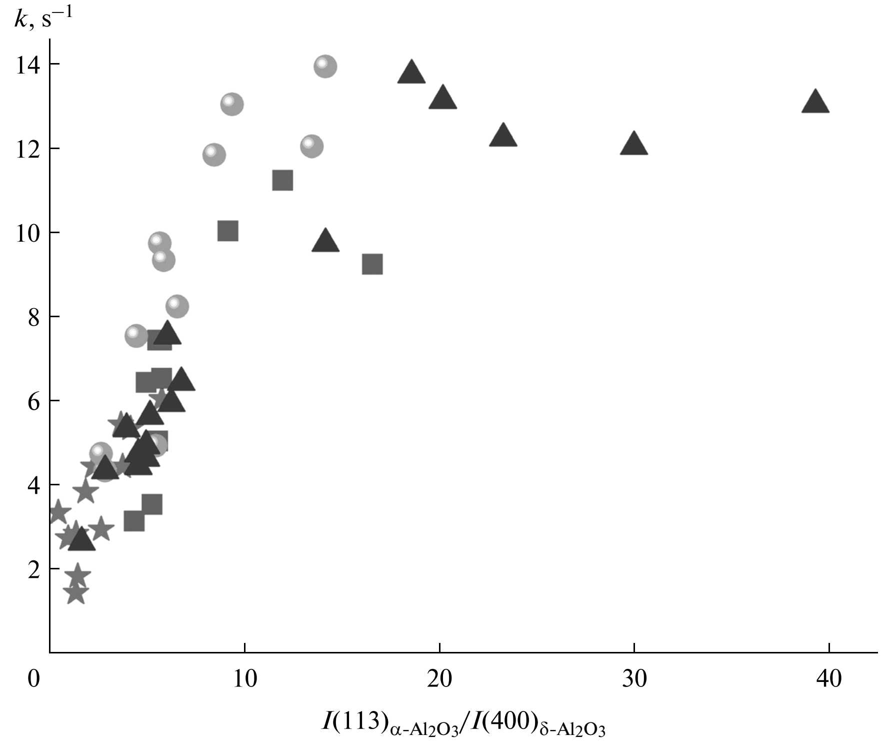

**Fig. 3.** Dependence of the catalytic activity of the $MnO_x$–$Al_2O_3$ samples on the degree of interaction. Sample series: (★) first, (■) second, (●) third, and (▲) fourth.

increased with the aluminum content of a mixture subjected to mechanochemical activation. In the simultaneous activation, the mutual diffusion of manganese and aluminum ions into the initial compounds occurred in addition to the crushing of particles and the formation of different types of defects. Thus, the aluminum-containing reactant was activated in the mixture on mechanochemical activation; this facilitated its conversion into corundum upon high-temperature treatment. With an increase in the relative concentration of the aluminum-containing precursor in the mechanochemically activated component, its fraction in the catalyst composition increased (correspondingly, the fraction of nonactivated AlOOH decreased, see Fig. 6); consequently, the degree of their interaction and the catalytic activity increased. Obviously, the components interacted more strongly on mechanochemical activation than in the absence of mechanochemical activation; thus, the relative fraction of the mechanically activated mixture was increased, and the degree of interaction increased subsequently on calcination.

Based on the experimental results, it is possible to conclude that, in general, the simultaneous activation of the Mn- and Al-containing components more strongly increased the catalytic activity of the samples, as compared with the activation of only manganese oxide. However, the use of the simultaneous mechanochemical activation of a mixture of manganese oxide with a manganese salt and aluminum hydroxide led to the more intense mixing and dispersion (because of their smaller hardness in comparison with that of corresponding oxides). As a result, fine particles of manganese oxide appeared in the catalyst prepared, and the increase in the catalytic activity was related to the presence of these particles.

Thus, we studied the possibility of preparing $MnO_x$–$Al_2O_3$ catalysts with the introduction of an additional stage of the mechanochemical activation of the reactants. In this work, we obtained four sample series by an extrusion method with the introduction of the following mechanically activated components into the paste of aluminum hydroxide: manganese oxide (series 1), a mixture of manganese oxide with aluminum oxide (series 2), manganese oxide with aluminum hydroxide (series 3), and manganese oxide with a manganese salt and aluminum hydroxide (series 4). We found that the characteristics of catalysts changed depending on treatment conditions.

The use of preliminarily activated reactants in the preparation of catalysts leads to the strengthening of interactions between components. We found that the catalytic activity of $MnO_x$–$Al_2O_3$ is determined by the degree of interaction of the initial reactants, whose value correlates with the amount of the active constituent $\beta$-$Mn_3O_4$.

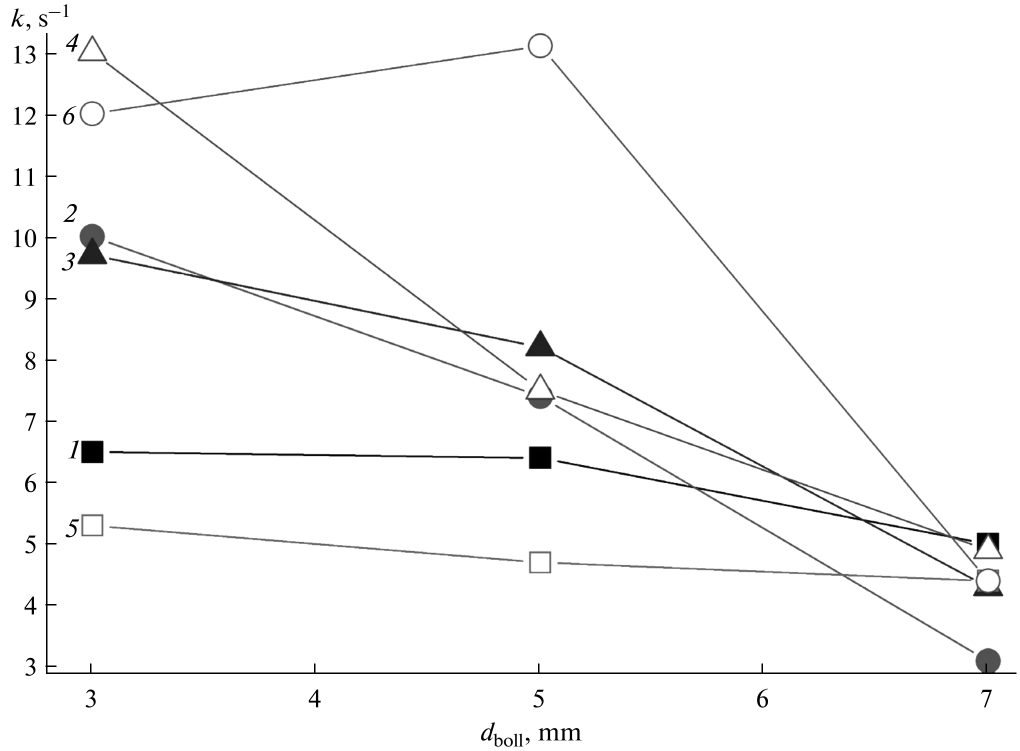

**Fig. 4.** Dependence of the catalytic activity of the $MnO_x$–$Al_2O_3$catalysts on the diameter of grinding balls for the following samples: (*1*) 2.5, 2.3, and 2.1; (*2*) 2.6, 2.4, and 2.2; (*3*) 3.5, 3.3, and 3.1; (*4*) 3.6, 3.4, and 3.2; (*5*) 4.8, 4.7, and 4.6; and (*6*) 4.17, 4.15, and 4.6.

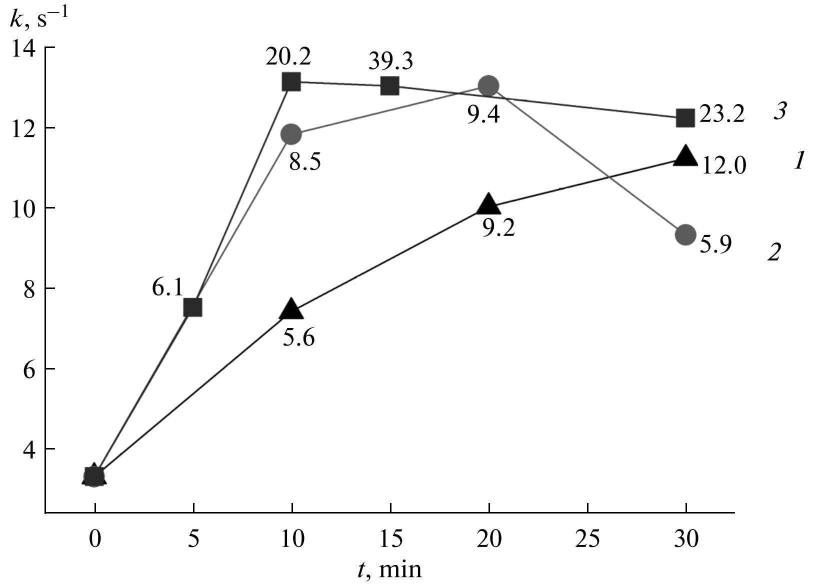

**Fig. 5.** Dependence of the catalytic activity of $MnO_x$–$Al_2O_3$ on the duration of mechanochemical activation for the following samples: (*1*) 2.7, 2.6, and 2.8; (*2*) 3.7, 3.6, and 3.8; and (*3*) 4.9, 4.15, 4.13, and 4.10. The degrees of interaction are specified at the curves.

We found that the conditions of mechanochemical activation can be chosen to ensure the best interaction between manganese- and aluminum-containing components by decreasing the sizes of grinding bodies, optimizing the duration of mechanochemical activation, and using the simultaneous activation of the manganese- and aluminum-containing components. On mechanochemical activation, the reactant parti-

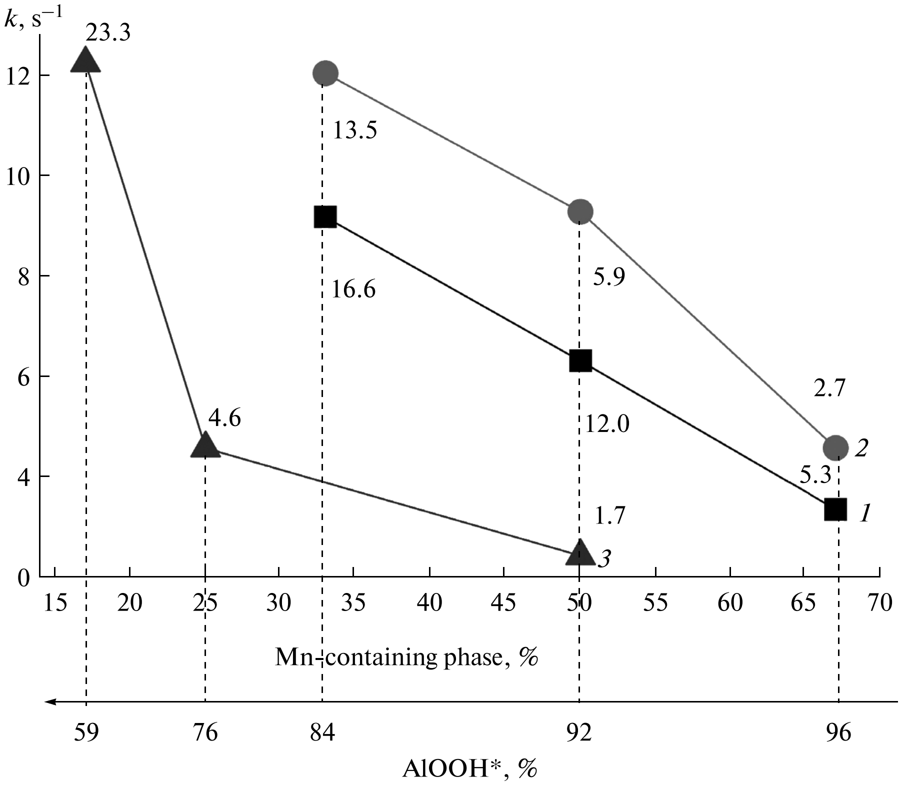

**Fig. 6.** Dependence of the catalytic activity of $MnO_x$–$Al_2O_3$ on the amount of a manganese-containing phase in the mechanochemically activated mixtures of the following samples: (*1*) 2.10, 2.3, and 2.9; (*2*) 3.10, 3.8, and 3.9; and (*3*) 4.10, 4.7, and 4.11. The concentrations of nonactivated AlOOH* are also specified (in % on a basis of the hydroxide introduced into the mechanochemically activated component). The degrees of interaction are specified at the curves.

cles are ground and the reaction $2MnO_2 \rightleftarrows Mn_2O_3 + 0.5O_2$ occurs in both forward and reverse directions with a change in the relative concentrations of $MnO_2$ and $Mn_2O_3$.

We established that intermediate calcination at 700°C should be avoided because $Mn_2O_3$ is formed in this case and the particles are enlarged; these particles less actively interact with the aluminum-containing precursor on calcination. However, under specific conditions of mechanochemical activation, it is possible to decrease the particle sizes without an increase in the $Mn_2O_3$ content. The use of the simultaneous activation of components facilitates the interaction between them to increase the catalytic activity of the samples.

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