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Fuel Combustion Reactions and Catalysts: XXI. Synthesis and Characterization of Modified Mn–Al–O Catalysts for High-Temperature Oxidation

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Abstract—The phase composition of supported Mn–Al–O catalysts and their activity in the reaction of methane oxidation were studied depending on the composition of aluminum oxide supports (γ-Al_2O_3 with different χ-Al_2O_3 contents modified with individual Mg, La, and Ce oxides or Mg + La and Mg + Ce oxide mixtures) and calcination temperatures (500, 900, and 1300°C). It was found that the Mn–Al–O catalysts based on γ-alumina containing χ-Al_2O_3 and modified with Mg, La, or Ce additives are more active and thermally stable (up to 1300°C) than the samples based on pure γ-Al_2O_3. A conclusion was drawn that a higher degree of disorder of the structure of χ-Al_2O_3, compared to that of γ-Al_2O_3, is favorable for a deeper interaction of manganese and modifying additives with the support at the early stages of the synthesis and for the formation of Mn–Al compounds with complex composition (solid solutions and/or hexaaluminates) at 1300°C. These compounds are responsible for the stability and high activity of the catalysts in methane oxidation.

INTRODUCTION

Transition metal oxides are well known as highly efficient catalysts for deep oxidation. Their reactivity depends on the metal–oxygen bond energy. Cobalt, copper, and manganese oxides [1] are most active, and they compete with catalysts based on noble metals in a number of processes. However, practical applications of bulk (unsupported) oxide catalyst are restricted by their inadequate performance characteristics, such as specific surface area, mechanical strength, and thermal stability. At the same time, these problems can be solved in principle, as was demonstrated using bulk copper oxide as an example [2, 3].

The formation of catalysts at the surface of a support with specified physicochemical, structural, and mechanical characteristics is the most commonly used method for producing and improving oxide catalysts. In this case, the activity per unit total surface area of the catalyst decreases compared with a bulk oxide. However, the activity per unit weight of the catalyst can be commensurable with that of bulk samples at a much lower concentration of the active component [2, 4, 5].

Although the metal–oxygen bond strength in manganese oxide is lower than that in cobalt or copper oxides [1], catalysts based on manganese oxide are most promising for use in high-temperature processes because of their comparatively high thermal stability. Thus, according to published data [6], bulk hopcalite ($CuO : MnO_2 = 1 : 2$) and 40 wt % hopcalite mixed with aluminum oxide retained sufficiently high activity in butane combustion after calcination at 800–1000°C. In this case, it was found that the temperature required for 50% butane conversion on a hopcalite–alumina sample was lower than that on bulk hopcalite; the corresponding values were equal to ~250 and ~300°C (for samples calcined at 800°C) or ~370 and ~450°C (for samples calcined at 1000°C), respectively.

This is associated with a specific feature of the Mn–Al–O system: an increase in the catalytic activity after the thermal treatment of MnO_x/γ-Al_2O_3 or MnO_x/α-Al_2O_3 samples at 900–1000 or 700–1000°C, respectively. Tsyrul'nikov *et al.* [7] found that the dispersion of the active component on the surface of the support is responsible for the thermal activation. This property of the above systems served as a basis for the development of a technology for producing an IKT-12-40 commercial Mn–Al–O catalyst [8], which exhibits high activity in complete oxidation reactions up to 1000°C.

According to published data [7, 8], a dispersed phase with an approximate composition of $Mn_3O_{4.2}$ and with a defect spinel structure is the active component of the Mn–Al–O system in the synthesis of which low-temperature alumina species are used. The α-Al_2O_3 phase plays a crucial role in the formation of the dispersed phase at temperatures lower than 1000°C; the formation of the former phase at the specified temperatures is stimulated by a mineralizing effect of supported manganese. However, this dispersed phase transformed to a more crystallized and less active phase of Mn_3O_4 after calcination above 1000°C.

According to the cited data, the use of α-Al_2O_3 as a starting support in place of γ-Al_2O_3 at temperatures higher than 850°C did not result in an increase in catalyst activity.

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Data on the modification of the Mn–Al–O system by the addition of rare earth oxides and other metal oxides, which is a well-known procedure for improving the thermal stability of γ-alumina [9, 10], are limited; a weak positive effect of some additives up to 750–800°C was mentioned [7, 8].

Presently, the development of efficient and stable catalysts for oxidation processes performed at 1200–1300°C is a topical problem in the high-temperature combustion of, for example, methane-containing raw materials. To improve oxide catalysts, it is reasonable to enhance the thermal stability and to retain the high activity of the Mn–Al–O system over the specified temperature range; this system is the most active oxide system at least at 900–1000°C.

Previously [11, 12], we found that the use of γ-alumina containing disordered χ-Al_2O_3 and modified with La, Ce, and Mg oxide additives as a support for Mn–Al–O catalysts is a promising direction for improving these catalysts.

In this work, in order to optimize the composition of an Mn–Al–O catalyst for high-temperature operation conditions (up to 1300°C), we analyzed the phase composition of modified Mn–Al–O catalysts and studied their activities in deep oxidation reactions depending on the concentration of a χ-Al_2O_3 phase in the starting support, the chemical nature of the modifying additive, and the temperature of calcination.

EXPERIMENTAL

The Mn–Al–O catalysts were prepared by the incipient wetness impregnation of a support with a manganese nitrate solution followed by drying and calcination in air at a specified temperature for 4 h. The manganese content of all the catalysts was equal to ~5 wt % (on a MnO_2 basis).

Spherical alumina based on γ-Al_2O_3 with different concentrations of χ-like Al_2O_3, which was prepared by hydrocarbon–ammonia molding [10], was used as a support (**1**, pure γ-Al_2O_3; **2**, 15% χ-Al_2O_3; and **3**, 35% χ-Al_2O_3). The main characteristics (specific surface areas and pore structures) of the supports were similar. Supports **1**–**3** were modified with Mg, La, and Ce oxide additives in accordance with the published procedure [12].

The catalytic activity was characterized by the following two parameters: (1) the reaction rate of butane oxidation at 400°C ($w \times 10^2$, $cm^3\ g^{-1}\ s^{-1}$) in a flow-circulation unit at an initial hydrocarbon concentration of 0.5 vol % and a circulation rate of 1000 l/h and (2) the temperature of 50% methane oxidation in a flow unit at the molar ratio CH_4 : air = 1 : 99 and a space velocity of 1000 h^{-1}.

The Mn, Mg, La, and Ce contents of the samples (wt % on an oxide basis) were determined by chemical analysis. The specific surface areas (S_{sp}, m^2/g) of the samples were measured from the thermal desorption of argon. X-ray diffraction (XRD) analysis was performed on an HZG-4 apparatus (CuK_α radiation) in the region $2\Theta = 10°–70°$ at a rate of 1 deg/min. X-ray spectrum microanalysis (MnK_α and AlK_α radiation spectra) was performed on an MAP-3 instrument with a probe diameter of ~1 μm at a voltage of 25 kV and a current of 30–40 nA.

RESULTS AND DISCUSSION

Catalysts on an unmodified support. According to XRD data (Table 1), when manganese was supported on pure (unmodified) support **1**, a highly dispersed phase of MnO_2 (sample no. 1) was formed on the surface of γ-Al_2O_3 after calcination at 500°C. In the case of support **2**, along with the MnO_2 phase, support line broadening was observed, which can be indicative of the beginning of the interaction of the support with manganese cations (sample no. 7). This interaction became stronger as the χ-Al_2O_3 content was increased (support **3**), as evidenced by broader lines of the support and a change in its lattice parameter as compared with the initial value (sample no. 12). In this case, a crystallized manganese oxide phase was not detected. This was likely due to the formation of a solid solution of manganese in the structure of the support.

An increase in the temperature of calcination to 900°C resulted in the appearance of an α-Al_2O_3 phase (1–4%) in all the test systems, and the support was a mixture of δ- and γ-alumina species (no more than 30% δ-Al_2O_3). It is likely that manganese ions occurred in solid solutions based on δ- and α-Al_2O_3. As mentioned previously [7, 8], the formation of an α-Al_2O_3 phase at 900°C resulted from a mineralizing effect of manganese additives on γ-alumina and indirectly evidenced the occurrence of interactions between the additive and the support.

The absence of individual manganese oxide phases from both sample no. 1 (due to a solid-phase reaction between MnO_2 and γ-Al_2O_3) and catalyst sample no. 12 (due to the perfection of the structure of a low-temperature solid solution of manganese in (γ,χ)-Al_2O_3) is also indicative of the interaction of manganese with the support at 900°C. However, a phase of β-Mn_2O_3 was detected in catalyst no. 7 at 900°C, and this fact may suggest that the solid-phase interaction of MnO_2 with the support, which exhibited signs of a low-temperature solid solution after 500°C, was hindered, as compared with the interaction of MnO_2 with γ-Al_2O_3 in the case of support **1**.

At 1300°C, α-Al_2O_3 and high-temperature Mn-containing phases (partially inverted spinel (Mn,Al)[Mn, $Al]_2O_4$ and spinel (Mn, Al)$[Al]_2O_4$) were detected in all the samples. Both of the spinels occurred in commensurable amounts on supports **1** and **2**, whereas the inverted spinel was mainly formed in the case of support **3**.

Table 1. Phase composition of Mn–Al–O catalysts (~5 wt % Mn on an MnO_2 basis)

Sample no.	Modifying additive, wt %	Phase composition		
		500°C	900°C	1300°C
		Support **1** (γ-Al_2O_3)		
1	–	MnO_2 ($D \sim 80$ Å) + γ-Al_2O_3 ($a \sim 7.910$ Å)	α-Al_2O_3 (~1%) + (δ^* + γ^*)-Al_2O_3	α-Al_2O_3 + (Mn, Al)$[Al]_2O_4$ ($a \sim 8.125$ Å) (Mn, Al) + [Mn, Al$]_2O_4$ ($a \sim 8.290$ Å)
2	MgO-4.5	β-Mn_2O_3 ($D \sim 180$ Å) + γ^*-Al_2O_3 ($a \sim 7.952$ Å)	γ^*-Al_2O_3 ($a \sim 7.956$ Å)	α-Al_2O_3 + (Mn, Mg)$[Al]_2O_4$ + ($a \sim 8.147$ Å)
3	MgO-4.5 La_2O_3-5	β-Mn_2O_3 ($D \sim 180$ Å) + γ^*-Al_2O_3 ($a \sim 7.952$ Å)	γ^*-Al_2O_3 ($a \sim 7.963$ Å)	–
4	MgO-4.5 La_2O_3-12	γ^*-Al_2O_3 ($a \sim 7.952$ Å)	γ^*-Al_2O_3 ($a \sim 7.970$ Å)	α-Al_2O_3 + (Mn, Mg)$Al_{11}LaO_{19}$
5	MgO-4.5 CeO_2-5	β-Mn_2O_3 ($D \sim 50$ Å) + CeO_2 + γ^*-Al_2O_3 ($a \sim 7.952$ Å)	CeO_2 + γ^*-Al_2O_3 ($a \sim 7.963$ Å)	CeO_2 + α-Al_2O_3 + traces (Mn, Mg)$[Al]_2O_4$ ($a \sim 8.140$ Å)
6	MgO-4.5 CeO_2-12	β-Mn_2O_3 ($D \sim 50$ Å) + CeO_2 + γ^*-Al_2O_3 ($a \sim 7.952$ Å)	CeO_2 + γ^*-Al_2O_3 ($a \sim 7.970$ Å)	–
		Support **2** (85% γ-Al_2O_3 + ~15% χ-Al_2O_3)		
7	–	MnO_2 ($D = 80$ Å) + an X-ray amorphous structure similar to γ-Al_2O_3 ($a \sim 7.910$ Å)	β-Mn_2O_3 + α-Al_2O_3 (~2%) + (δ^* + γ^*)-Al_2O_3	α-Al_2O_3 + (Mn, Al)$[Al]_2O_4$ ($a \sim 8.097$ Å) (Mn, Al) + [Mn, Al$]_2O_4$ ($a \sim 8.285$ Å)
8	MgO-4.5	β-Mn_2O_3 ($D \sim 180$ Å) + γ^*-Al_2O_3 ($a \sim 7.952$ Å)	α-Al_2O_3 (traces) + γ^*-Al_2O_3 ($a \sim 7.965$ Å)	α-Al_2O_3 + traces (Mn, Mg)$[Al]_2O_4$ ($a \sim 8.130$ Å)
9	MgO-4.5 La_2O_3-5	γ^*-Al_2O_3 ($a \sim 7.952$ Å)	γ^*-Al_2O_3 ($a \sim 7.956$ Å)	α-Al_2O_3 + (Mn, Mg)$Al_{11}LaO_{19}$
10	MgO-4.5 La_2O_3-12	γ^*-Al_2O_3 ($a \sim 7.952$ Å)	γ^*-Al_2O_3 ($a \sim 7.956$ Å)	α-Al_2O_3 (traces) + traces (Mn, Mg)$[Al]_2O_4$ ($a \sim 8.120$ Å) (Mn, Mg)$Al_{11}LaO_{19}$
11	MgO-4.5 CeO_2-5	CeO_2 + γ^*-Al_2O_3 ($a \sim 7.952$ Å)	CeO_2 + γ^*-Al_2O_3 ($a \sim 7.956$ Å)	CeO_2 + α-Al_2O_3 + (Mn, Mg)$[Al]_2O_4$ ($a \sim 8.127$ Å)
		Support **3** (65% γ-Al_2O_3 + ~35% χ-Al_2O_3)		
12	–	X-ray amorphous structure similar to γ-Al_2O_3, ($a \sim 7.917$ Å)	α-Al_2O_3 (~4%) + (δ^* + γ^*)-Al_2O_3	α-Al_2O_3 + (Mn, Al)$[Al]_2O_4$ ($a \sim 8.117$ Å) (Mn, Al) + [Mn, Al$]_2O_4$ ($a \sim 8.277$ Å)
13	MgO-4.5	γ^*-Al_2O_3 ($a \sim 7.952$ Å)	α-Al_2O_3 (traces) + γ^*-Al_2O_3 ($a \sim 7.963$ Å)	–
14	MgO-4.5 La_2O_3-5	″	γ^*-Al_2O_3 ($a \sim 7.967$ Å)	α-Al_2O_3 + (Mn, Mg)$[Al]_2O_4$ ($a \sim 8.113$ Å) + (Mn,Mg)$Al_{11}LaO_{19}$
15	MgO-4.5 La_2O_3-12	″	″	–
16	MgO-4.5 CeO_2-5	CeO_2 ($D \sim 60$Å) + γ^*-Al_2O_3 ($a \sim 7.952$ Å)	CeO_2 ($D \sim 90$ Å) + γ^*-Al_2O_3 ($a \sim 7.971$ Å)	CeO_2 ($D \sim 500$ Å) + α-Al_2O_3 + (Mn, Mg)$[Al]_2O_4$ ($a \sim 8.123$ Å) + traces (Mn, Mg)$Al_{11}CeO_{19}$
17	MgO-4.5 CeO_2-12	CeO_2 + γ^*-Al_2O_3 ($a \sim 7.952$ Å)	CeO_2 + γ^*-Al_2O_3 ($a \sim 7.964$ Å)	CeO_2 + α-Al_2O_3 + (Mn, Mg)$[Al]_2O_4$ ($a \sim 8.123$ Å) + (Mn, Mg)$Al_{11}CeO_{19}$

Note: γ^*-Al_2O_3 is a solid solution based on the spinel structure of γ-Al_2O_3 with the unit cell parameter a (Å) given in parentheses, and δ^*-Al_2O_3 is a solid solution based on δ-Al_2O_3.

Catalysts on a support modified with lanthanum or cerium. On modification with lanthanum (5 and 12 wt % La_2O_3), lattice parameters in the Mn–Al–O catalysts prepared on supports **1**–**3** at 500 and 900°C practically corresponded to that of the initial support regardless of the concentration of the χ-Al_2O_3 phase in it. In this case, crystallized Mn-containing phases were not observed. At 1300°C, the mixed hexaaluminate $MnLaAl_{11}O_{19}$ was formed. The mineralizing effect of manganese was suppressed, and the α-Al_2O_3 phase appeared only at 1300°C.

On modification with cerium (5 and 12 wt % CeO_2), changes in the lattice parameter of the initial support upon the introduction of manganese were also insignificant in the catalysts on supports **1**–**3** at 500 and 900°C. Crystallized Mn-containing phases were also not detected. Up to 1300°C, the oxide CeO_2 was present in all the samples. As demonstrated using sample no. 16 (Table 1) as an example, the particle size of this oxide increased with temperature. In this case, as well as in the modification with lanthanum, the α-Al_2O_3 phase was observed only at 1300°C. Moreover, mixed hexaaluminate traces (probably, $MnAl_{11}CeO_{19}$) were detected at 1300°C in samples on supports **2** and **3** containing the χ-Al_2O_3 phase with an increased cerium content.

Catalysts on a support modified with magnesium. On the modification of supports **1**–**3** with magnesium, the interactions of manganese cations with alumina were of another character, and they considerably depended on the phase composition of the initial support. Thus, according to data given in Table 1, a coarsely dispersed phase of β-Mn_2O_3 was formed simultaneously with a solid solution of magnesium in alumina on the surface of supports **1** and **2** at 500°C (sample nos. 2, 8). Only in the case of support **3**, Mn-containing phases were absent (sample no. 13). As the temperature was increased to 900°C, the perfection of a solid solution took place, and its lattice parameter increased. In all cases, crystallized Mn oxide species were absent; this fact is indicative of an increase in the interaction of Mn^{3+} with Al_2O_3 in the presence of an alumina–magnesium solid solution. At 1300°C, two phases were observed: α-Al_2O_3 and the mixed solid solution (Mn, Mg)$[Al]_2O_4$, whose lattice parameter corresponds to ~50% substitution of manganese for magnesium.

Catalysts on a support modified with Mg + La or Mg + Ce additives. On the modification of Mn–Al–O catalysts based on supports **1**–**3** with Mg + La or Mg + Ce additives, the mechanisms of formation of phase compositions were the same as in the case of the samples modified with only magnesium. However, the presence of La or Ce enhanced the interaction of manganese cations with the support. Thus, at 500°C, the oxide phase β-Mn_2O_3 appeared only in samples prepared on support **1** (Table 1, sample nos. 3, 5, and 6), whereas manganese oxide phases were not detected in analogous catalysts on supports **2** (sample nos. 9–11) and **3** (sample nos. 14–17). Note that crystallized Mn-containing phases were absent from sample no. 4, which contained 12% La.

At 900°C, the perfection of mixed solid solutions took place with an increase in their lattice parameters, and manganese oxide phases were absent from all the samples. As in the case of catalysts modified with individual La and Ce oxides, at this temperature the α-Al_2O_3 phase was absent from all the above Mg–La- and Mg–Ce-containing catalysts (Table 1). This is due to the stabilizing effect of La and Ce additives on the thermal stability of alumina [12].

After calcination at 1300°C, the α-Al_2O_3 phase was observed in all the catalysts modified with the two oxides. Manganese-containing compounds in catalysts with Mg–La additives comprised the hexaaluminate (Mn, Mg)$Al_{11}LaO_{19}$, whereas they comprised the spinel-based solid solutions (Mn, Mg)$[Al]_2O_4$ in the samples with Mg–Ce oxides. In this case, the lattice parameters of the solid solutions corresponded to 25–40% substitution of manganese for magnesium in spinel. In the Mg–La samples on supports **2** and **3** containing χ-Al_2O_3, traces of the solid solutions (Mn, Mg)$[Al]_2O_3$ were detected, whereas a phase of the hexaaluminate (Mn, Mg)$Al_{11}CeO_{19}$ was found in the Mg–Ce samples (Table 1).

X-ray spectrum microanalysis. The results of X-ray spectrum microanalysis provided support for conclusions that the interaction of manganese with the support in the presence of the χ-Al_2O_3 phase increased with concentration of this phase. Thus, no interaction between manganese oxide and alumina was detected in the near-surface layer of an unmodified Mn–Al–O catalyst on support **1**, which contained no χ-Al_2O_3 (Fig. 1, **A**), at 500°C (the MnK_α and AlK_α spectra profiles were opposite). After catalyst calcination at 900°C, a correlation between the positions of minimums and maximums in the MnK_α and AlK_α spectra was observed, which was indicative of weak interactions between these components. At 1300°C, the bonding of the Mn-containing phase formed to the support was noticeably weakened, and the distribution of this phase over the support surface was nonhomogeneous. In unmodified catalysts on supports **2** and **3**, which contained χ-Al_2O_3 (Fig. 1, **M**), the character of the MnK_α and AlK_α spectra even at 500°C was indicative of the occurrence of interaction between manganese and aluminum oxides, and this interaction increased with calcination temperature.

Activity of the catalysts in the reaction of butane oxidation. Table 2 summarizes data on the specific surface areas and activities of the test catalysts in the oxidation reaction of butane. The specific surface areas of all the catalysts decreased with calcination temperature. However, note that the absolute values of surface areas at 1300°C were higher for modified catalysts except for sample nos. 10 and 11, which were modified with cerium. According to data given in Table 1, this

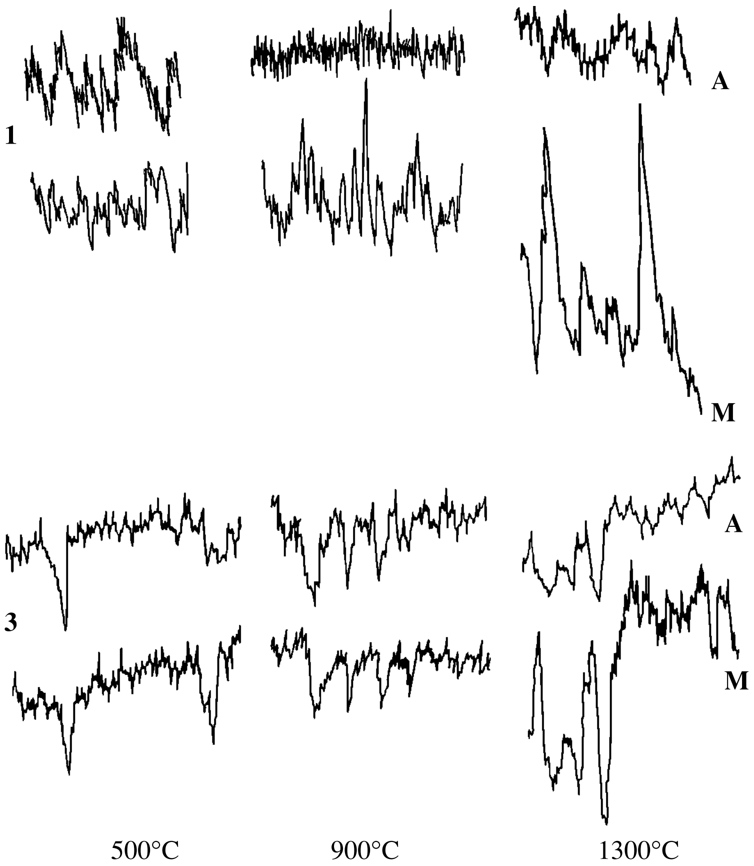

Fig. 1. X-ray spectrum microanalysis data: (**A**) AlK_α and (**M**) MnK_α radiation intensities for unmodified Mn–Al–O catalysts prepared on supports **1** and **3** and calcined at 500, 900, and 1300°C (the MnK_α intensity was represented on a scale 20 times greater than that for AlK_α).

deviation could be due to the formation of coarsely dispersed CeO_2 at this temperature.

Catalyst nos. 1–3 calcined at 500°C exhibited approximately equal activities regardless of the χ-Al_2O_3 content of the support. After treatment at 900°C, an increase in the activity (or thermal activation [7, 8]) was observed, which was most significant in sample no. 3, which had a high χ-Al_2O_3 content.

The effect of thermal activation at 900°C was insignificant in catalysts modified with magnesium (sample nos. 4–6), although a weak effect of the χ-Al_2O_3 phase present in the support did occur. Lanthanum additives (sample nos. 7–9) noticeably increased the activity of catalysts calcined at 500°C; however, the activity of these samples after calcination at 900°C was lower than that of unmodified catalysts. Analogous changes in the activity were also observed in Ce-containing catalysts (sample nos. 10, 11); however, in this case, the absolute values of the activities of samples calcined at 500°C were lower than in La-containing catalysts.

After calcination at 1300°C, the activity of catalysts decreased regardless of their composition. In this case, the catalysts on supports **2** and **3** were several times more active than samples with similar compositions prepared on support **1**.

Activity of the catalysts in the reaction of methane oxidation. Figure 2 displays data on the catalytic activity of Mn–Al–O samples prepared based on modified supports **2** and **3** and calcined at 1300°C in the reaction of methane oxidation. For these samples, the temperature of 50% methane conversion was 520–550°C; this value is lower than that for an IKT-12-40 commercial catalyst, whose manganese content was twofold greater [8], by 80–110°C. In this case, a catalyst based on support **3** modified with an Mg + Ce additive exhibited the highest activity (as well as in butane oxidation, see Table 2, sample no. 16). Note that an increase in the manganese content of the modified catalysts to a level of IKT-12-40 (~10 wt % on an MnO_2 basis) decreased the temperature of 50% methane conversion by ~20–30°C.

Thus, the Mn–Al–O catalysts prepared based on γ-alumina containing χ-Al_2O_3 and modified with Mg, La, or Ce additives are more active and thermally stable (up to 1300°C) compared with samples based on pure γ-Al_2O_3, including the IKT-12-40 catalyst [8]. Note that only the presence of a χ-Al_2O_3 phase in the starting sup-

Table 2. Specific surface areas and activities of Mn–Al–O catalysts of different composition in the deep oxidation of butane (~5 wt % Mn on an MnO_2 basis)

Sample no.	Composition of the support		S_{sp} (m^2/g) after calcination			$w \times 10^2$ ($cm^3 g^{-1} s^{-1}$) after calcination		
	starting support (phase composition)	modifying additive, wt %	500°C	900°C	1300°C	500°C	900°C	1300°C
1	**1** (γ-Al_2O_3)	–	176	105	3.2	0.52	0.85	0.08
2	**2** (85% γ-Al_2O_3 + 15% χ-Al_2O_3)	–	192	115	2.3	0.47	1.41	0.18
3	**3** (65% γ-Al_2O_3 + 35% χ-Al_2O_3)	–	222	112	–	0.52	1.58	–
4	**1**	MgO-4.5	156	110	4.0	0.45	0.44	0.09
5	**2**	″	165	108	4.3	0.43	0.64	0.58
6	**3**	″	190	105	–	0.69	0.71	–
7	**1**	La_2O_3-5	138	102	4.3	1.70	0.78	0.08
8	**2**	″	164	114	3.9	1.86	0.91	0.67
9	**3**	″	187	134	3.7	1.41	0.72	0.46
10	**1**	CeO_2-5	139	91	0.6	1.51	0.80	0.02
11	**2**	″	160	115	2.6	1.21	0.89	0.50
12	**1**	MgO-4.5 La_2O_3-5	119	81	9.7	1.00	0.48	0.10
13	**2**	″	150	108	6.3	1.70	0.60	0.32
14	**3**	″	155	112	6.9	1.20	0.60	0.44
15	**2**	MgO-4.5 CeO_2-5	153	100	3.5	1.02	0.58	0.28
16	**3**	″	158	103	4.9	1.00	0.59	0.82

port or the modification of γ-Al_2O_3 with the above additives does not produce the desired effects. We believe that a higher degree of disorder of the structure of χ-Al_2O_3, compared with γ-Al_2O_3, is favorable for deeper interactions of manganese and modifying agents with the support at the early stages of the synthesis and for the production of high-temperature Mn–Al compounds of complex composition (solid solutions and/or hexaaluminates) at 1300°C. These compounds are responsible for the stability and high activity of the modified Mn–Al–O catalysts in methane oxidation.

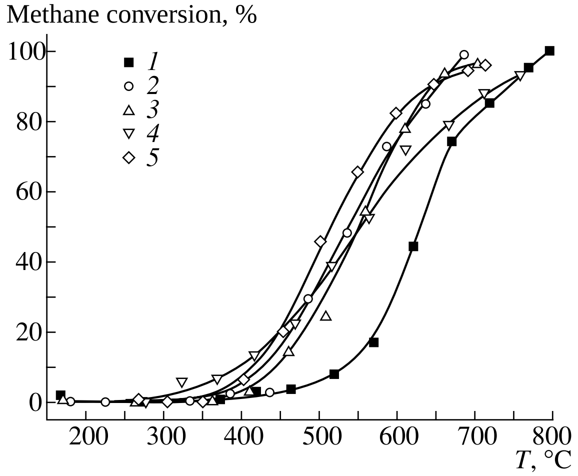

Fig. 2. Activity of Mn–Al–O catalysts calcined at 1300°C in the reaction of methane oxidation: (*1*) IKT-12-40, (*2*) Mn/support **2** + La_2O_3, (*3*) Mn/support **2** + MgO, (*4*) Mn/support **2** + CeO_2, and (*5*) Mn/support **3** + (MgO + CeO_2).

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REFERENCES

1. Popovskii, V.V., *Doctoral (Chem.) Dissertation*, Novosibirsk: Inst. of Catalysis, 1973.
2. Tsikoza, L.T., *Cand. Sci. (Chem.) Dissertation*, Novosibirsk: Inst. of Catalysis, 1980.
3. USSR Inventor’s Certificate no. 609 549, *Byull. Izobret.*, 1978, no. 21.
4. USSR Inventor’s Certificate no. 810 256, *Byull. Izobret.*, 1981, no. 9.

5. USSR Inventor's Certificate no. 787082, *Byull. Izobret.*, 1980, no. 46.
6. Jaworska-Golas, Z., Mista, W., Wrzyszcz, J., and Zawadzki, M., *Catal. Lett.*, 1994, vol. 24, no. 1, 2. p. 133.
7. Tsyrul'nikov, P.G., Sal'nikov, V.S., Drozdov, V.A., Stuken, S.A., Bubnov, A.V., Grigorov, E.I., Kalinkin, A.V., and Zaikovskii, V.I., *Kinet. Katal.*, 1991, vol. 32, no. 2, p. 439.
8. RF Patent 2063803, 1996.
9. Shaper, H. and Doesburg, E.B.M., *Appl. Catal.*, 1983, vol. 7, no. 2, p. 221.
10. Ismagilov, Z.R., Shkrabina, R.A., and Koryabkina, N.A., *Catal. Today,* 1999, vol. 47, nos. 1–4, p. 51.
11. Tsykoza, L.T., Shkrabina, R.A., Koryabkina, N.A., Ushakov, V.A., Shikina, N.V., and Ismagilov, Z.R., *Proc. 7th Nordic Symp. on Catal., Åbo/Turku, Finland*, 1996, p. 32.
12. Tsykoza, L.T., Ismagilov, Z.R., Shkrabina, R.A., Koryabkina, N.A., Shikina, N.V., Arendarskii, D.A., Ushakov, V.A., and Kalinkin, A.V., *Memorial G.K. Boreskov Conf.*, Novosibirsk, 1997, part 2, p. 410.