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High-temperature catalysts with a synergetic effect of Pd and manganese oxides

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Abstract

A synergetic effect in the catalytic activity has been found after palladium introduction in Mn–Al–O systems. The magnitude of the synergetic effect depends on the types of the oxidic manganese species: oxide Mn_3O_4, spinel (Mn, Mg)[Mn, Al]$_2O_4$ or hexaaluminate (Mn, Mg)$LaAl_{11}O_{19}$. The synergetic effect of Pd and manganese-containing compounds is observed only if palladium is introduced to the low-temperature precursor of the manganese alumina spinel or manganese hexaaluminate. The synergetic effect is not observed when high-temperature samples with formed spinel or hexaaluminate phases are modified with Pd.

Keywords: Methane combustion; Bicomponent catalyst; Manganese oxides; Hexaaluminate; Manganese–alumina spinel; Palladium oxide; Synergetic effect

1. Introduction

Catalytic combustion of fuels is regarded as an attractive alternative to flame combustion. Catalytic combustion provides high combustion efficiency and low emission of air pollutions such as NO_x, CO, and unburned hydrocarbons [1–3]. At present, house hold appliances [4], catalytic boilers [5,6], gas turbines [2,7–12] and technical processes [4,6,13] have commercial potential for applications of catalytic combustion.

The catalytic materials must be active and stable in a wide temperature range from 500 to 1300 °C in order to ensure effective combustion of hydrocarbon fuel, including low-calorie fuel (or lean mixtures), in stable operation. At high temperatures, the catalysts are required to maintain a high surface area and catalytic activity, and to have high thermal shock resistance. On the other hand, the catalysts must have a low light-off temperature.

The existing catalysts for high-temperature combustion of hydrocarbon fuel may be divided into two categories: (1) catalysts based on noble metals, mostly Pd and Pt; (2) catalysts based on transition metal oxides, mostly, spinels, perovskites and hexaaluminates.

Among the catalysts of the first group, catalysts containing Pd are the most active in oxidation of methane [7] and unsaturated hydrocarbons [14]. Pd catalysts are more stable than Pt catalysts with respect to thermal sintering in the oxidizing environment. The upper temperature limit of their use is about 950–1000 °C [15,16]. However, the use of Pd at temperatures above 800 °C is limited due to PdO conversion to Pd metal at 750–800 °C, which has lower activity in oxidation reactions than PdO [17].

Among the catalysts of the second group, manganese oxides are the most promising material for synthesis of high-temperature catalysts due to high thermal stability of supported Mn oxides [18–20] and significant increase of the catalytic activity in deep oxidation of hydrocarbons, e.g. n-C_4H_{10}, benzene and cumene [18], observed after calcination at 900–1100 °C (called a thermal activation effect [18]). The thermal stability of manganese–alumina catalysts can be increased (up to 1300 °C) by doping with lanthanum, magnesium or cerium oxides [19,21], particularly, using disordered alumina for synthesis of the catalysts [21]. In this case, high-temperature Mn and Al compounds can be formed, e.g. spinels, perovskites and hexaaluminates of various compositions. This provides high thermal stability of manganese–alumina catalysts [19,21]

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and contributes to the overall activity of the catalysts [9,10]. In a number of studies it has been reported that partial substitution of the Al site in the hexaaluminate lattice by a Mn cation results in improvement of the oxidation activity without lowering the heat resistance [9,10,22]. Lanthanum–strontium–manganese and barium–manganese hexaaluminates has been recognized as some of the successful designs in hexaaluminate catalysts [9,10,12,22–25].

Considering of numerous publications on performance of Pd catalysts supported on pure alumina we conclude that potentialities of improving of thermal stability and combustion activity of this system (Pd/Al_2O_3) are mostly limited. During synthesis of high-temperature catalysts it is necessary to take into account that it is important to secure uniform distribution and high dispersity of the supported active component on the support to obtain materials with high reactive surface area at high temperatures. One of the technical solutions of this problem is synthesis of spinels and/or hexaaluminates having crystal lattices with strict positions of cations, e.g. Mn^{n+} ions. Manganese hexaaluminate having high thermal stability and sufficient specific surface area [9,10,23] can be used to support Pd and simultaneously contribute to the reactivity of the whole catalytic system. In addition, a synergetic effect is observed in hydrocarbon oxidation reactions, methane oxidation in particular [7,26–32], for most low-temperature catalytic systems containing a noble metal and a transition metal oxide [14,26–29]. This effect may be important for development of catalysts for high-temperature fuel combustion processes as well.

In this work we have studied the main physicochemical and catalytic properties of high-temperature catalysts containing Pd and/or manganese oxides in methane oxidation as a function of the type of the manganese-containing compound (MnO_x, $MnAl_2O_4$, $MnLaAl_{11}O_{19}$), palladium concentration (0.2–2 wt.%) and palladium deposition sequence. X-ray diffraction (XRD), X-ray microanalysis, and TPR have been used for characterization of the catalysts and understanding of the synergetic effect of Pd and manganese hexaaluminate.

2. Experimental

2.1. Alumina materials

Granulated alumina was prepared by hydrocarbon-ammonia moulding from pseudoboehmite aluminum, drying and calcination at 550 °C [33].

Granulated alumina modified by magnesium oxide (2.8 wt.%) was also used for hexaaluminate preparation. The modifying additive was introduced by immersion of ‘‘raw’’ granule of pseudoboehmite aluminum into magnesium nitrate solution followed by drying and calcination at 550 °C [33].

For both types of granulated aluminas, XRD phase composition was 85–90% of γ-Al_2O_3 and 10–15% of χ-Al_2O_3, the specific surface area was close to 170 m^2/g, and the total pore volume, 0.5 cm^3/g.

2.2. Catalyst preparation

2.2.1. Pd catalyst supported on ($\gamma + \chi$)-Al_2O_3

The Pd catalysts were prepared by wet impregnation of granulated ($\gamma + \chi$)-Al_2O_3 by chloropalladic acid solution, drying at 110 °C and annealing in air at 600, 900 and 1200 °C for 4 h. The Pd loading ranged from 0.25 to 2 wt.%. The specific surface areas of the samples calcined at 900 and 1200 °C were 90 and 12 m^2/g, respectively.

2.2.2. Manganese oxides catalysts supported on ($\gamma + \chi$)-Al_2O_3

Two series of supported manganese oxides catalysts were prepared.

The first series were manganese-containing catalysts supported on pure granulated ($\gamma + \chi$)-Al_2O_3. The catalysts were prepared by wet impregnation of granulated ($\gamma + \chi$)-Al_2O_3 with a manganese nitrate solution followed by drying at 110 °C. The catalysts were calcined at 500 and 900 °C or 1200 °C for 4 h. The manganese loading was 5 or 10 wt.% MnO_2. The type of manganese oxide: MnO_2, Mn_2O_3, Mn_3O_4 or $MnAl_2O_4$, was regulated by calcination of the air-dried catalysts at different temperatures. The specific surface areas of the samples calcined at 900 and 1200 °C were in the range of 85–90 and 3.8–5.5 m^2/g, respectively.

The second series were manganese-containing catalysts supported on granulated ($\gamma + \chi$)-Al_2O_3 modified by lanthanum and/or magnesium oxide. These catalysts contained $MnLaAl_{11}O_{19}$ or (Mg, Mn)$LaAl_{11}O_{19}$ hexaaluminates as the main active component.

The hexaaluminate catalysts of composition $MnLaAl_{11}O_{19}$ were prepared by successive wet impregnation of granulated ($\gamma + \chi$)-Al_2O_3 with lanthanum and manganese nitrate solutions followed by drying at 110 °C and calcination at 500 °C. The La_2O_3 loading was 5–18 wt.%, and the MnO_2 loading was 3–10 wt.%. For hexaaluminate formation the samples were calcined at 1200 °C for 4 h. The specific surface area was in the range of 12–14 m^2/g.

The hexaaluminate catalysts of composition (Mg, Mn) $LaAl_{11}O_{19}$ were prepared with using granulated ($\gamma + \chi$)-Al_2O_3 modified by MgO. The lanthanum oxide and manganese (as MnO_2) loadings introduced by wetness impregnation were 18 and 2–2.3 wt.%, respectively. The calcination temperature was 1200 °C. The specific surface area was equal to 14 m^2/g.

2.2.3. Supported PdMn oxide catalysts

Manganese–alumina catalysts prepared by methods described above were used for synthesis of binary PdMn catalysts. Manganese–alumina catalysts and manganese hexaaluminates were doped with palladium by impregnation of the low-temperature catalysts with chloropalladic acid of desired concentration followed by calcination at 600, 900 and 1200 °C. The Pd concentration in the catalysts was 0.25, 0.5, 1 and 2 wt.%.

Catalysts with Pd (0.5 wt.%) introduced after calcination of the manganese–alumina catalyst at 1200 °C were prepared for comparison.

The catalysts are denoted as xPd/yMnO$_2$/zLa$_2$O$_3$/Al$_2$O$_3$-T, where x, y and z are Pd, MnO$_2$ and La$_2$O$_3$ loadings (in wt.%), T is calcination temperature (in °C).

2.3. Physicochemical methods

The contents of Mn, La, Mg oxides and Pd were determined by atomic absorption spectroscopy with inductively coupled plasma (AAS-ICP), employing a BLYRD analyzer.

The XRD analysis of the samples was carried out using a HZG-4C (Freiberger Prazisionmechanik) diffractrometer with monochromatic Cu Kα irradiation. The phase compositions were determined using diffraction patterns recorded in the 2θ range 10–70°. The diffraction patterns were identified using the JCPDS database [34].

Temperature-programmed reduction (TPR) experiments were carried out using 10% H$_2$ in Ar with a flow of 40 ml/min in a laboratory instrument equipped with a thermal conductivity detector. The temperature was raised from 25 to 900 °C with 10 °C/min rate. Before performing the TPR experiments, the samples were first pretreated in oxygen at 500 °C for 30 min and cooled to room temperature, then flushed with Ar flow. The weight of the samples was 100 mg and the particle size was 250–500 μm. Water produced during the TPR experiment was removed using a cold trap. Calibration for the hydrogen consumption was carried out by CuO reduction.

The distribution of Mn and Pd on the catalyst surface was studied using a MAP-3 microanalyzer. The samples were anchored in epoxy resin and polished. The probe diameter was 2 mm, the working voltage was 25 kV. Al Kα, Mn Kα, Pd Kα lines were analyzed.

Specific surface areas (S_{BET}, m^2/g) of the samples were determined using thermal desorption of argon.

2.4. Catalytic activity tests

The catalytic activity in methane oxidation was studied using a flow reactor in the temperature range of 200–700 °C at a space velocity of 1000 and 24,000 h^{-1}. The methane concentration in the feed was 1 vol.% in air. The granulated catalyst in amount of 1 cm^3 was used in the experiments. The catalytic activity was characterized by the temperature at which 50% methane conversion was achieved ($T_{50\%}$).

3. Results and discussion

To determine the synergetic effect of Pd and manganese oxides in deep oxidation of methane, three types of catalysts were prepared, and their catalytic and physicochemical properties were studied:

- Pd catalysts supported on ($\gamma + \chi$)-Al$_2$O$_3$;
- Manganese–alumina catalysts containing MnO$_x$, MnAl$_2$O$_4$ or MnLaAl$_{11}$O$_{19}$ as the active component;
- Binary catalysts containing Pd and MnO$_x$, MnAl$_2$O$_4$ or MnLaAl$_{11}$O$_{19}$;

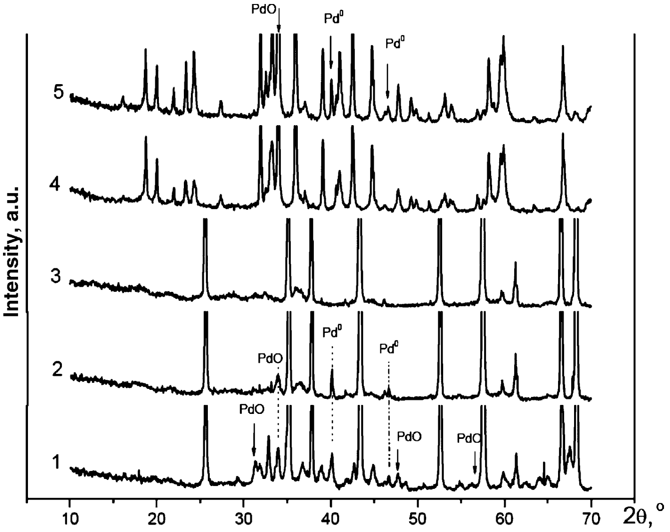

Fig. 1. XRD patterns of catalysts supported on alumina and calcined at 1200 °C for 4 h: 0.8Pd/Al$_2$O$_3$ (1), 0.8Pd/4.8MnO$_2$/Al$_2$O$_3$ (2), 4.8MnO$_2$/Al$_2$O$_3$ (3), 4.9MnO$_2$/2.8MgO–18La2O3/Al$_2$O$_3$ (4), and 1.5Pd/4.9MnO$_2$/2.8MgO–18La$_2$O$_3$/Al$_2$O$_3$ (5). Unmarked XRD peaks are α-Al$_2$O$_3$ on 1–3 curves and hexaaluminate on 4, 5 curves.

- Below we shall discuss the physicochemical and catalytic properties of these types of catalysts individually.

3.1. Catalytic properties of Pd catalysts supported on ($\gamma + \chi$)-Al$_2$O$_3$

According to the XRD data, a well-crystallized PdO phase with large particle size (>30 nm) and Pd metal are present in the catalysts with Pd loading above 0.5 wt.% after calcination at 1200 °C (Fig. 1, curve 1). A wide hydrogen H$_2$-consumption peak at 80–200 °C corresponding to reduction of PdO particles is observed in the TPR spectrum of 0.8Pd/γ-Al$_2$O$_3$ catalyst calcined at 600 °C (Fig. 2, curve 1). The PdO particles are, most

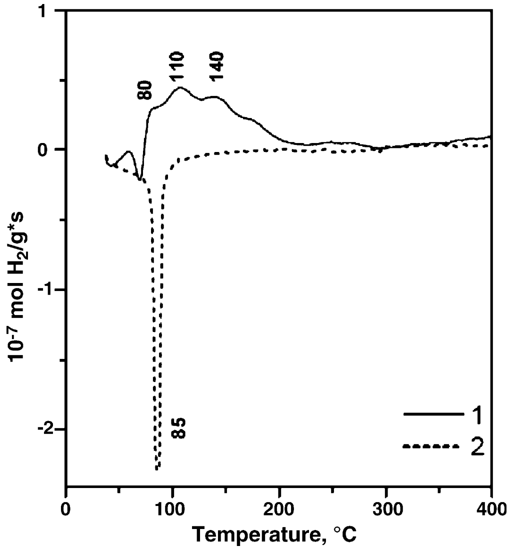

Fig. 2. TPR spectra of 0.8 Pd/Al$_2$O$_3$ catalyst calcined at 600 °C (1) and 1200 °C (2).

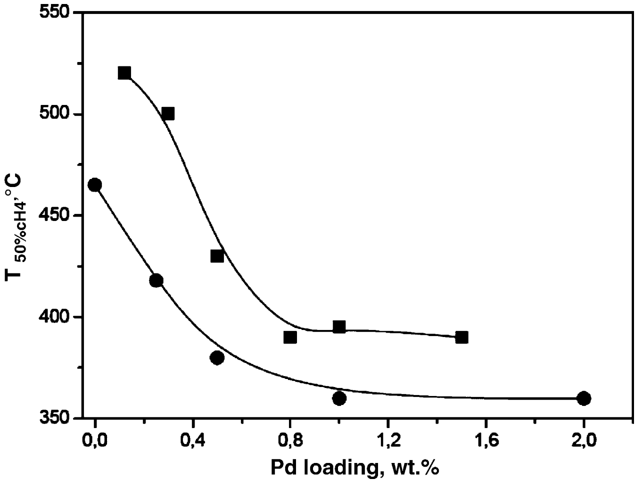

Fig. 3. Temperature of 50% methane conversion ($T_{50\%\,CH_4}$) on Pd catalysts supported on alumina (■) or $3MnO_2/2.8MgO–18La_2O_3/Al_2O_3$ (●) vs. Pd loading. The catalysts were calcined at 1200 °C for 4 h. Test conditions: 1 vol.% CH_4 in air, 1000 h^{-1}.

likely, observed in the TPR spectra of this catalyst calcined at 1200 °C as a week wide H_2-consumption peak in the temperature range of 200–300 °C (Fig. 2, curve 2). Also a hydrogen desorption peak at 78–86 °C is observed in the TPR spectra (Fig. 2, curve 2). Comparison of the TPR spectra of the catalysts calcined at 600 and 1200 °C suggests that the observed hydrogen desorption peak is due to the presence of Pd metal particles. This assumption is in good agreement with the results reported by Farrauto et.al. [17] and Lyubovsky co-workers [35] who observed irreversible PdO conversion to Pd during calcination of supported Pd/Al_2O_3 catalysts in air at 800–900 °C. PdO conversion to Pd is usually considered to be the cause of the methane oxidation activity decrease with the temperature increase [17]. However, it has been shown that the catalytic activity in methane oxidation grows after PdO conversion to Pd metal, especially at elevated temperatures [35].

The experimental data on the catalytic activity of Pd catalysts supported on γ-Al_2O_3 after high-temperature annealing at 1200 °C for 4 h are shown in Fig. 3 for different Pd concentrations (0.12–1.5 wt.%). One can see that the catalytic activity in methane oxidation grows when the Pd concentration increases from 0.12 to 0.8 wt.%. Meanwhile, the temperature of 50% methane conversion ($T_{50\%\,CH_4}$) decreases from 520 to 390 °C (Fig. 3). Note that the increase of the calcination temperature of 0.8Pd/γ-Al_2O_3 catalyst from 600 to 1200 °C results in the increase of its catalytic activity in methane oxidation that is observed as an decrease of 50% methane conversion temperature from 430 to 390 °C.

3.2. Physicochemical and catalytic properties of manganese–alumina catalysts

Two series of manganese–alumina catalysts containing MnO_x, $MnAl_2O_4$, $MnLaAl_{11}O_{19}$ as the active component and their catalytic performance in methane oxidation will be discussed. The desired crystalline phase of manganese-containing compounds was obtained by varying the manganese concentration (3–10 wt.%), concentration of the modifying agents (MgO and La_2O_3) added to the alumina supports (5–21 wt.%) and the final calcination temperature.

3.2.1. Influence of the calcination temperature

Table 1 presents the phase compositions of two manganese–alumina catalysts supported on alumina as a function of the annealing temperature (the first series). The active component of the catalyst with 5 wt.% MnO_2 after calcination at 500 °C consists of highly dispersed MnO_2. The increase of the calcination temperature to 900 and 1200 °C results in successive phase transformation of MnO_2 to β-Mn_2O_3 and Mn_3O_4. The phase transformations of manganese oxides are made more complicated by the interaction of MnO_2 and β-Mn_2O_3 with alumina to form a solid solution of Mn^{3+} cations in γ-Al_2O_3 (a = 7.93–8.17 Å), which decomposes at 1200 °C to

Table 1
XRD composition and catalytic activity of the supported manganese–alumina catalysts calcined at different temperature

No.	Catalyst	Manganese loading, wt.% as MnO_2	Calcination temperature (°C)	XRD composition	S_{BET} (m^2/g)	Temperature of X% CH_4 conversion[a] (°C)	
						$T_{50\%\,CH_4}$	$T_{50\%\,CH_4}$
1	$5MnO_2/Al_2O_3$	5.4	500	γ^*-Al_2O_3 ($a \sim 7.910$ Å); MnO_2 ($D \sim 80$ Å)	130	485	570
			900	α-Al_2O_3 + δ^*-Al_2O_3; γ^*-Al_2O_3 ($a \sim 7.93$–7.94 Å); β-Mn_3O_4	82	400	465
			1200	α-Al_2O_3; (Mn, Al)[Al]$_2O_4$ ($a \sim 8.097$ Å); (Mn, Al)[Mn]$_2O_4$ ($a \sim 8.285$ Å)	3.8	530	660
2	$10MnO_2/Al_2O_3$	9.45	500	γ^*-Al_2O_3 ($a \sim 7.910$–8.115 Å); MnO_2 ($D \sim 200$ Å); β-Mn_2O_3 ($D \sim 300$ Å)	115	445	535
			900	α-Al_2O_3 + θ-Al_2O_3; γ^*-Al_2O_3 ($a \sim 7.93$–8.17 Å); β-Mn_3O_4	75	420	525
			1200	α-Al_2O_3; (Mn, Al)[Al]$_2O_4$ ($a \sim 8.078$ Å); (Mn, Al)[Mn]$_2O_4$ ($a \sim 8.27$ Å)	3.0	575	700

γ^*-Al_2O_3 and δ^*-Al_2O_3 are solid solution of Mn^{3+} in structure of γ-Al_2O_3 and δ-Al_2O_3, respectively (Mn, Al)[Mn]$_2O_4$ are Mn_3O_4 spinel doped Al^{3+} cations or solid solution of Al^{3+} in structure of Mn_3O_4 spinel.

[a] Measured at 1000 h^{-1}, 1 vol.% CH_4 in air.

α-Al_2O_3 (Fig. 1, curve 3) and manganese-aluminum spinel (Mn, Al)[Al]$_2$O$_4$ (normal spinel, a = 8.078 Å). Note that Mn_3O_4 spinel, most likely, is doped with Al^{3+} cations (solid solution of Al^{3+} cations in spinel structure of Mn_3O_4) (Mn, Al)[Mn]$_2$O$_4$ as indicated by the lattice parameters (a = 8.285 Å). It is in a good agreement with [36]. The authors of [36] have observed a phase transformation of MnO_x/Al_2O_3 system starts at 950 °C with the formation of a metastable non-stoichiometric manganese–alumina cubic spinel and nonequilibrium solid solution of Mn^{3+} ions in the structure of γ-Al_2O_3, which decomposes to α-Al_2O_3 modified by Mn^{3+} ions and nanocrystalline β-Mn_3O_4 particles doped with Al^{3+} ions.

The increase of the manganese concentration in the catalyst to 10 wt.% leads to the formation of large quantities of well-crystallized oxide compounds with particle size ~20–30 nm. In addition to crystallized MnO_2 phase, the diffraction pattern contains peaks characteristic of β-Mn_2O_3 and a solid solution based on Al_3O_3 spinel structure with the lattice parameter a ~8.115 Å even after calcination at 500 °C. A calcination temperature increase results in the phase transformation of manganese oxides to Mn_3O_4 and perfection of the solid solution of Mn^{3+} in the Al_2O_3 structure with the formation of (Mn, Al)[Al]$_2$O$_4$ spinel.

Fig. 4 presents the TPR profiles for 5% MnO_2/Al_2O_3 catalyst annealed at various temperatures from 500 to 1300 °C. The chosen calcination temperature range may be divided into three regions where the catalytic activity is significantly different (Table 1). In the 500–800 °C calcination temperature range the catalysts shows the methane oxidation activity typical for oxide catalysts. The TPR spectra of the sample calcined at 500 °C (Fig. 4, curve 1) is characterized by three H_2-consumption peaks at 330, 400 and 445 °C, and H_2/Mn molar ratio equal to 0.85. The increase of the calcination temperature to 600–800 °C is accompanied by the disappearance of the peak at 330 °C, a slight shift of the peaks at higher temperatures to 445–485 °C (Fig. 4, curve 2) and a decrease of the H_2/Mn molar ratio to 0.54–0.58. Comparison of the TPR and XRD data indicates that in the low-temperature catalysts calcined at 500 °C manganese mostly exists as MnO_2. During the TPR experiment it is reduced first to Mn_2O_3 (330 °C), then to Mn_3O_4 (400 °C) and to MnO (445 °C). In the catalysts annealed at 600–800 °C manganese is stabilized as Mn_2O_3 with, most likely, larger particle size than in the catalysts calcined at 500 °C. These TPR profiles of low-temperature supported MnO_x catalysts are similar to those exhibited by bulk manganese oxides [37,38] and MnO_x crystallites on the alumina surface [14,38,39].

As shown previous publications [18,19,21,36], the increase of the calcination temperature of manganese–alumina catalysts from 500 to 900 °C results in an increase of their activity in methane [19,21], n-C_4H_{10} [18] and CO [36] oxidation. For instance, $T_{50\%\,CH_4}$ was about 400 and 485 °C, respectively, for 5% Mn/Al_2O_3 samples calcined at 900 and 500 °C [19]. According to the XRD data (Table 1) the active component of the former catalyst consists of Mn_3O_4 doped by Al^{3+} and solid solution of Mn^{3+} ions in the structure of γ-Al_2O_3, about 70–80% of all manganese atoms being in the Mn_3O_4 spinel. The sample calcined at 900 °C is characterized by a wide H_2-consumption peak in the low-temperature region of the TPR spectrum (150–500 °C, Fig. 4, curve 3), which splits into three peaks at 170, 265 and 410 °C when the calcination temperature is increased to 1000–1100 °C (Fig. 4, curve 4).

Further increase of the calcination temperature to 1200 and 1300 °C leads to a decrease of the catalytic activity (Table 1) and shift of the TPR peaks to higher temperatures (Fig. 4, curves 5 and 6), which indicates that the formed manganese-containing compounds are more difficult to reduce. The H_2/Mn molar ratio in the TPR spectra of the catalysts annealed at 1000–1300 °C was 0.45–0.42. Comparison of the TPR and XRD data shows that easily (170–270 °C) and difficultly (310–480 °C) reducible compounds correspond to Mn_3O_4

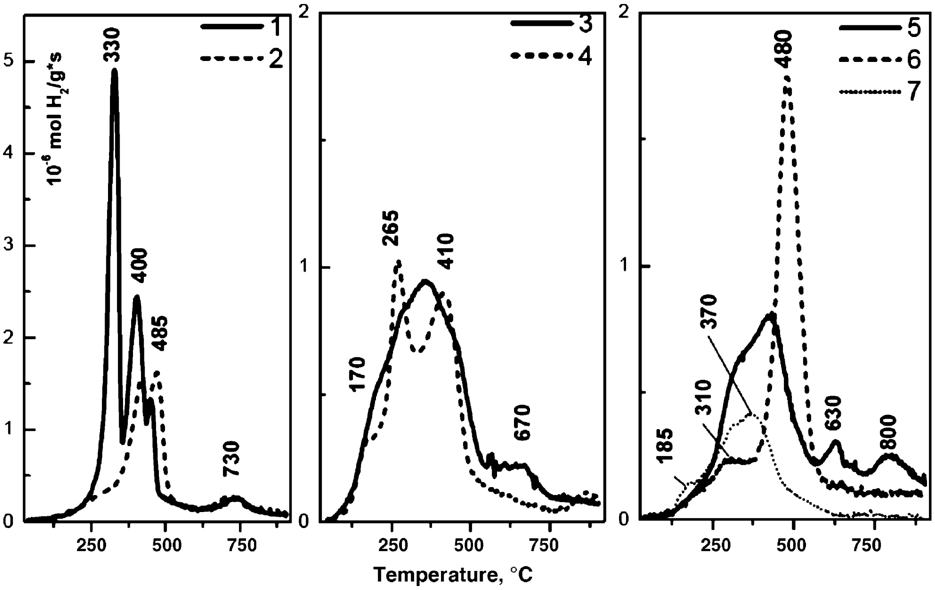

Fig. 4. TPR spectra of $5MnO_2/Al_2O_3$ catalyst calcined at 500 °C (1), 800 °C (2), 900 °C (3), 1100 °C (4), 1200 °C (5), and 1300 °C (6). TPR spectrum of catalysts with the structure of hexaaluminates (Mn, Mg)$LaAl_{11}O_{19}$ (7).

spinel doped with Al^{3+} cations and (Mn, Al)[Al]$_2$O$_4$ spinel doped with Mn^{3+} cations, respectively. Taking into account the data reported in [36], the TPR peak in the temperature range around 480 °C or higher might be also due to reduction of Mn^{3+} cations in α-Al_2O_3 structure. The analysis of the physico-chemical and catalytic properties of the samples annealed at 900–1100 and 1200–1300 °C leads to a conclusion that Mn_3O_4 spinel has higher catalytic activity. This conclusion agrees well with the results reported by Tsyrulnikov et al. [36]. It was shown in [36] that the formation of nanocrystalline particles of β-Mn_3O_4 phase doped with Al^{3+} ions during calcination of the MnO_x/Al_2O_3 system at 950 °C leads to a sharp increase of the activity in deep hydrocarbon oxidation reactions.

3.2.2. *Influence of the modifying agents*

Table 2 summarizes the crystalline phases identified by XRD for Mn catalysts supported on alumina modified by La and Mg oxide (the second series). α-Al_2O_3, hexaaluminate and spinel (Mg, Mn)Al_2O_4 are the main crystalline phase observed in the samples calcined at 1200 °C. Perovskite-type oxides, such as $LaMnO_3$ or $LaAlO_3$, were not detected. The data reported in Table 2 show that it is possible to change the ratio of the spinels and hexaaluminate formed in the catalyst after calcination at 1200 °C by varying the atomic (Mn + Mg)/La ratio. Manganese oxide introduced in the amount exceeding the stoichiometric (Mn + Mg)/La ratio is stabilized after the high-temperature annealing as (Mg, Mn)[Al]$_2$O$_4$ spinel. Its lattice parameter grows with the manganese concentration (Table 2).

When the sample with the La loading around 18–21 wt.% La_2O_3 and atomic ratio (Mn + Mg)/La equal to 1 was calcined at 1200 °C, the hexaaluminate phase was only one observed by XRD. These samples were characterized by a number of intensive XRD diffraction peaks at $2\theta = 32.0°$, 33.9°, 36°, 39.2°, 42.7°, 44.9°, 60.0°, and 67° (Fig. 1, curve 4). Hexaaluminates based on $LaAl_{11}O_{18}$, $MnLaAl_{11}O_{19}$ and $MgLaAl_{11}O_{19}$ are characterized in the JCPDS database by a practically the same set of diffraction peaks with similar intensities. Thus, the analysis of the XRD spectra indicates that high-temperature catalysts doped with magnesium appear to contain a hexaaluminates with different composition. As for manganese oxide, Mn_2O_3 is known to be transformed into Mn_3O_4 above ca. 1000 °C. The diffraction peak characteristic of Mn_3O_4 is at $2\theta = 36.1°$, 32.3° and 28.9°, numbers in parentheses are relative intensities. Although two intense peaks at 36.1° and 32.3° were superimposed on the peaks attributable to the hexaaluminate phase, the complete disappearance of the diffraction peak at 28.9° might mean that at these temperatures manganese oxide no longer exists in the form of Mn_3O_4. The lack of diffraction peaks typical for the spinel-type oxide ($2\theta = 30.8°$ and 64.2°), indicates that $MnAl_2O_4$ is not formed in this sample. Taking into account the fact that the crystallinity degree of hexaaluminate itself was poor, this suggests that supported manganese oxide reacts with alumina during calcination at high temperatures to form manganese-containing hexaaluminate at 1200 °C and above. Stabilization of rare earth elements, e.g. La^{3+} and/or Mg^{2+} cations, in a mixed solid solution based on the γ-Al_2O_3 structure in tetrahedral and octahedral positions, correspondingly, is known to limit substantially the diffusion of Al^{3+} ions leading to the formation of α-Al_2O_3 and result in the formation of hexaaluminates $MgLaAl_{11}O_{19}$ [40] and $La_2O_3{\cdot}11Al_2O_3$ [41] after calcination at high temperatures. A similar result was reported by Zhang et al. [42] who also observed the formation of La–β-Al_2O_3 phase doped at Mn^{2+} cation when the low-temperature sample with $La_2O_3{\cdot}19Al_2O_3$ composition was impregnated with manganese nitrate solution and calcined at 1000–1200 °C.

Table 2
XRD composition and catalytic activity of the supported manganese-lanthanum-alumina catalysts calcined at 1200 °C

No.	Catalyst	Chemical composition			XRD composition	S_{BET} (m^2/g)	Temperature of $X\%$ CH_4 conversion[a] (°C)	
		La_2O_3 (wt.%)	MnO_2 (wt.%)	(Mn + Mg)/La (at.%)			$T_{50\%\,CH_4}$	$T_{50\%\,CH_4}$
1	$3MnO_2/5La_2O_3/MgO–Al_2O_3$	5	3	3.5	α-Al_2O_3; (Mg, Mn)[Al]$_2$O$_4$, $a \sim 8.128$ Å; HAM[b], $d/n_{220} \sim 1.4004$ Å	9	470	560
2	$5MnO_2/5La_2O_3/MgO–Al_2O_3$	5	5	4.2	α-Al_2O_3; (Mg, Mn)[Al]$_2$O$_4$, $a \sim 8.128$ Å; HAM, $d/n_{220} \sim 1.4004$ Å	6	490	570
3	$7MnO_2/5La_2O_3/MgO–Al_2O_3$	5	7	5	α-Al_2O_3; (Mg, Mn)[Al]$_2$O$_4$, $a \sim 8{,}134$ Å; HAM, $d/n_{220} \sim 1.4004$ Å	14	520	600
4	$10MnO_2/5La_2O_3/MgO–Al_2O_3$	5	10	6.2	α-Al_2O_3; (Mg, Mn)[Al]$_2$O$_4$, $a \sim 8{,}166$ Å; HAM, $d/n_{220} \sim 1.4004$ Å	6	545	625
5	$5MnO_2/12La_2O_3/MgO–Al_2O_3$	12	5	1.7	α-Al_2O_3 (trace); (Mg, Mn)[Al]$_2$O$_4$, $a \sim 8.120$ Å; HAM, $d/n_{220} \sim 1.4004$ Å	9	480	570
6	$10MnO_2/12La_2O_3/MgO–Al_2O_3$	12	10	2.5	α-Al_2O_3 (trace); (Mn, Mg)[Al]$_2$O$_4$, $a \sim 8.171$ Å; (Mn, Al)[Mn, Al]$_2$O$_4$, $a \sim 8.276$ Å HAM, $d/n \sim 1.4011$ Å	7	520	600
7	$3.5MnO_2/18La_2O_3/MgO–Al_2O_3$	18	3.5	1.0	HAM, $d/n_{220} \sim 1.3993$ Å	14	460	560
8[c]	$3.5MnO_2/18La_2O_3/Al_2O_3$	18.9	10	1.0	HAM, $d/n_{220} \sim 1.4022$ Å	17	450	550

The granulated alumina modified by MgO (2.8 wt.%) were used for high-temperature catalyst preparation.

[a] Measured at 1000 h^{-1}, 1 vol.% CH_4 in air.

[b] HAM, $d/n_{220} \sim 1.4004$ Å is manganese hexaaluminate (Mg, Mn)$Al_{11}LaO_{19}$.

[c] Prepared on granulated alumina (without MgO addition).

The high-temperature samples (1200 °C) where manganese mostly exists as manganese hexaaluminate are characterized by a wide H_2-consumption peak with a maximum at 370 °C and H_2/Mn ratio in the range of 0.2–0.3 (Fig. 4, curve 7). It well known that Mn^{2+} cations in MnO are not reduced by hydrogen to metal until temperatures as high as 1700 °C [43]. Hence, it reasonable to assume that the H_2-consumption peak at 370 °C is due to Mn^{3+} cations doping the hexaaluminate structure.

Comparison of the catalytic activity of Mn–Al–O catalysts containing different high-temperature manganese compounds: (Mn, Mg)$[Al]_2O_4$ spinel and (Mn, Mg)$LaAl_{11}O_{19}$ hexaaluminate suggests that the formation of manganese hexaaluminate makes it possible to improve both the catalytic activity in methane oxidation and the thermal stability of the catalyst. For example, $T_{50\%\,CH_4}$ was equal to 530 °C (Table 1, no. 1) and 460 °C (Table 2, no. 7) for high-temperature (1200 °C) catalysts containing manganese as (Mn, Al)$[Al]_2O_4$ spinel and hexaaluminate, respectively. It should be noted that the catalytic activity of the samples based on $MnLaAl_{11}O_{19}$ (Table 2, no. 8) and (Mn, Mg)$LaAl_{11}O_{19}$ (Table 2, no. 7) hexaaluminates were identical at the same total concentration of the hexaaluminate phase in the catalyst, with $T_{50\%\,CH_4} = 450 - 460\,°C$.

Thus, according to the XRD data (Table 2), it has been shown that is possible to stabilize different oxidic manganese species by varying the synthesis conditions of manganese–alumina catalysts: manganese oxide loading, modification of the alumina with La_2O_3 or/and MgO and calcination temperature. The nature of the manganese compounds MnO_2, Mn_2O_3, Mn_3O_4, (Mn, Mg)Al_2O_4 or (Mn, Mg)$Al_{11}O_{19}$ determines the catalytic activity of the manganese–alumina catalysts and the temperature range of their use. As it will be shown below, the type of the manganese compound has a significant effect on the appearance of a synergetic effect in the catalytic activity of Pd-containing manganese–alumina catalysts.

3.3. Physicochemical and catalytic properties of supported PdMn oxides catalysts

Fig. 1 presents the XRD patterns of high-temperature catalysts containing manganese oxides with Pd. XRD composition are summarized in Table 3. High-temperature annealing of manganese–alumina catalysts doped with Pd can result in the formation of three main oxidic manganese phases. The type of the resulting phase is determined by the manganese loading, composition of the modifying additives and calcination temperature. As in the case of one-component catalysts, Mn_3O_4 spinel doped with Al^{3+} cations (or solid solution of Al^{3+} cations in Mn_3O_4 structure) is formed after calcination at 900 °C (Table 3, no. 1). Crystallized phases of (Mn, Al)$[Al]_2O_4$ spinel (Table 3, no. 2) and manganese hexaaluminate (Table 3, no. 3) are observed after calcination at 1200 °C. The optimum method to obtain manganese hexaaluminate is to add manganese, lanthanum and magnesium oxides in the atomic ratio (Mn + Mg)/La ~1 to the granulated $(\gamma + \chi)$-Al_2O_3 (Fig. 1, curve 5). Thus, the palladium introduction to the low-temperature manganese–alumina catalysts does not affect the formation of high-temperature manganese compounds.

According to the XRD data presented in Fig. 1, curves 2 and 5, palladium exists in high-temperature binary catalysts as PdO particles ($2\theta = 33.9°$) and Pd metal ($2\theta = 40.15°$). The ratio of PdO and Pd phases depends on the calcination temperature of the binary catalyst. At the same palladium concentration in the catalysts, the concentration of palladium metal grows with the calcination temperature increase from 900 to 1200 °C in good agreement with the results reported by Lyubovsky co-workers [35]. At the same palladium concentration in the catalysts, the amounts of PdO and Pd observed by XRD after calcination at 1200 °C are smaller in manganese–alumina samples (Fig. 1, curve 2, 0.8Pd/5MnO_2/Al_2O_3-1200) than in alumina ones (Fig. 1, curve 1, 0.8Pd/Al_2O_3-1200). So, it appears that introduction of manganese cations to alumina improves the PdO stability to reduction to Pd metal. The suppression of PdO dissociation was first observed for NiO addition to Al_2O_3 support [44]. It was found that PdO supported on Al_2O_3 and mixed Al_2O_3–36NiO oxides was completely reduced to Pd metal at 800 and 860 °C, respectively [44].

For convenience during discussion of the results of TPR and catalytic experiments let us divide high-temperature binary Pd–Mn catalysts into three groups: spinel-type oxide Mn_3O_4,

Table 3

XRD composition and catalytic activity of the binary Pd–Mn catalysts calcined at 1200 °C

No.	Catalyst	Chemical composition (wt.%)			T_{calc}[a] (°C)	S_{BET} (m^2/g)	XRD composition	Temperature of $X\%$ CH_4 conversion[b] (°C)	
		La_2O_3	MnO_2	Pd				$T_{50\%\,CH_4}$	$T_{50\%\,CH_4}$
1	0.5Pd/5MnO_2/Al_2O_3	–	2.74	0.57	900	85	α-Al_2O_3 + δ^*-Al_2O_3; γ^*-Al_2O_3; β-Mn_3O_4	340	450
2	0.5Pd/5MnO_2/Al_2O_3	–	2.74	0.57	1200	5.4	α-Al_2O_3; (Mn, Al)$[Al]_2O_4$, $a \sim 8.060$ Å; PdO (>300 Å) and Pd	415	515
3	0.5Pd–$MnLaAl_{11}O_{19}$	La_2O_3, 18.9; MgO, 2.8	1.98	0.58	1200	14	$MnLaAl_{11}O_{19}$ ($d/n_{220} = 1.3993$ Å); PdO (>300 Å) and Pd	360	420
4	0.5Pd/$MnLaAl_{11}O_{19}$	La_2O_3, 18.9; MgO, 2.8	1.98	0.53	500	12	$MnLaAl_{11}O_{19}$ ($d/n_{220} = 1.3993$ Å); PdO (>500 Å)	400	480
5	Pd/(Mn, Al)$[Al]_2O_4$	MgO, 2.8	3.28	0.5	500	2.4	α-Al_2O_3; (Mn, Al)$[Al]_2O_4$, $a \sim 8.125$ Å; PdO (>500 Å)	480	590

[a] Final calcination temperature of binary Pd–Mn catalysts.

[b] Measured at 1000 h^{-1}, 1 vol.% CH_4 in air.

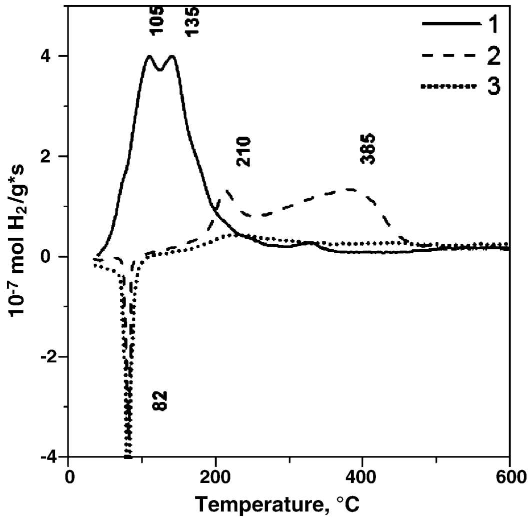

Fig. 5. TPR spectra of binary $0.5Pd/5MnO_2/Al_2O_3$ catalysts calcined at 500 °C (1) and 1200 °C (2). TPR spectrum of binary $1.5Pd/3MnO_2/2.8MgO–18La_2O_3/Al_2O_3$ catalysts with the structure of hexaaluminates (Mn, Mg)$LaAl_{11}O_{19}$ (3).

spinel-type oxide $MnAl_2O_4$, and hexaaluminate-type oxides $MnLaAl_{11}O_{19}$ and (Mn, Mg)$LaAl_{11}O_{19}$.

TPR profile of the binary Pd–Mn catalyst containing according to XRD spinel-type oxide Mn_3O_4 is presented in Fig. 5, curve 1. The TPR profile of binary Pd–Mn catalyst calcined at 900 °C only shows a H_2-consumption peak at around 105 °C with to reduction of PdO crystallites to Pd metal. The peak at 135 °C is due reduction of Mn^{3+} cation in Mn_3O_4 spinel to MnO. The weak peak at 330 °C should be ascribed to the reduction of large Mn_3O_4 particles to MnO or to the reduction of Mn^{3+} cations stabilized in the solid solution in the alumina structure.

TPR profiles of the binary Pd–Mn catalyst containing according to XRD spinel-type oxide $MnAl_2O_4$ and hexaaluminate-type oxide are presented in Fig. 5, curve 2 and curve 3, respectively. Independent of the type of the high-temperature manganese-containing compound, all binary Pd–Mn catalysts calcined at 1200 °C were characterized by H_2-desorption peak at 82 °C, related to Pd metal particles. Clear peaks at 170–265 °C observed in the TPR profile of binary Pd–Mn catalyst with spinel-type oxides (Fig. 5, curve 2) and manganese hexaaluminate (Fig. 5, curve 3) as the main active component are due to reduction of Mn^{3+} cation doping the structures of $MnAl_2O_4$ or α-Al_2O_3 and $MnLaAl_{11}O_{19}$. Note that for high-temperature binary Pd–Mn catalyst the H_2/Mn ratio varies in the range of 0.16–0.28, which is 3–10 times lower than for high-temperature Mn catalyst with similar phase composition.

So, the presence of Pd strongly affects the reduction profile of all catalysts containing different manganese oxides. The reduction temperature, the shape and the number of peaks are changed. Binary Pd–Mn catalysts containing spinel-type oxide Mn_3O_4 or manganese hexaaluminate are almost completely reduced at the temperature, at which the reduction of the samples consisting these Mn compounds alone is only starting. The TPR profile of binary Pd–Mn catalysts containing manganese–alumina spinel is also shifted to lower temperature. However, the shift is much smaller. The lower reduction temperature of MnO_x in the presence of Pd has been observed for binary Pd–Mn catalysts supported on Al_2O_3 and calcined at 800 °C [14], but has not been observed for the catalyst calcined at 350 °C [39]. The lower reduction temperature of MnO_x in the mixed samples is usually explained by two reasons [14]. Both require strong interaction between Pd and MnO_x. First, noble metals catalyze the reduction of MnO_x by hydrogen spill-over during the TPR experiment [14]. Second, the mobility of the lattice oxygen in MnO_x is increased [14].

Fig. 6A presents the data on the catalytic activity of high-temperature binary $0.5Pd/5MnO_2/Al_2O_3$ catalyst calcined at 900 °C. According to the XRD data, most of manganese in the manganese–alumina catalyst after calcination at 900 °C exists as spinel-type oxide Mn_3O_4 and a solid solution of Mn^{3+} in (γ + δ)-Al_2O_3 and is reduced in hydrogen at 135–170 °C. The palladium introduction (0.5 wt.%) to the low-temperature $5MnO_2/Al_2O_3$ catalyst makes it possible to increase its activity in methane oxidation. At 1000 h^{-1} the temperature of 50% methane conversion was 340 °C, which is lower by 60–70 °C than those of single-component $0.5Pd/Al_2O_3$ and $5MnO_2/Al_2O_3$ (Table 1, no. 1) samples calcined at 900 °C. Note that the largest differences in the activity of binary and single-component catalysts were observed at low temperatures and long contact times.

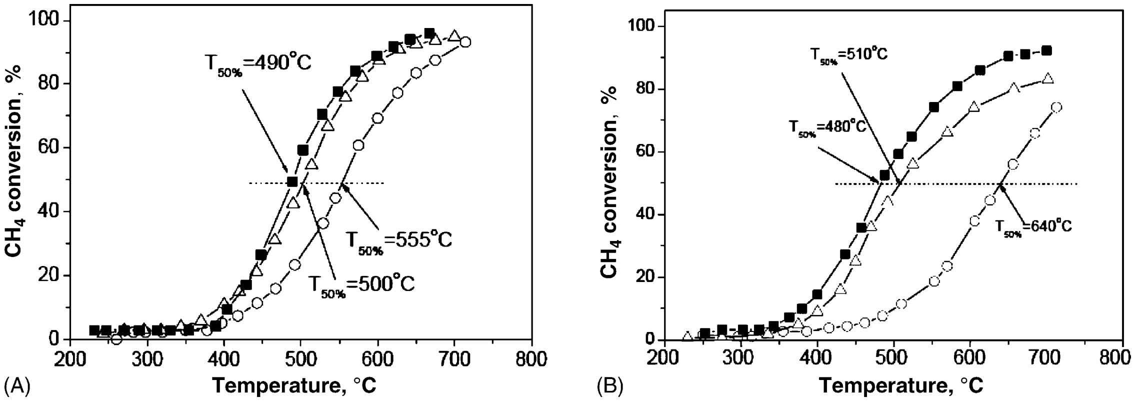

Fig. 6. Methane conversion over $5MnO_2/Al_2O_3$ (○), $0.5Pd/Al_2O_3$ (△) and $0.5Pd/5MnO_2/Al_2O_3$ (■) catalysts calcined at 900 °C (A) and at 1200 °C (B). Test condition: 1 vol.% CH_4 in air, 24,000 h^{-1}.

Fig. 6B shows the data on activity of high-temperature binary $0.5Pd/5MnO_2/Al_2O_3$ catalyst calcined at 1200 °C. According to the XRD data, most manganese in the manganese–alumina catalyst calcined at 1200 °C is in the form of spinel-type oxide (Mn, Al)$[Al]_2O_4$ of variable composition, which is reduced in hydrogen at 300–450 °C. Palladium addition to the low-temperature $5MnO_2/Al_2O_3$ catalyst followed by calcination at 1200 °C increases its methane oxidation activity. At 1000 h^{-1} the temperature of 50% methane conversion was 415 °C (Table 3, no. 2), which is lower by 115 °C than that of single-component $5MnO_2/Al_2O_3$ sample (Table 1, no. 1) calcined at 1200 °C. However, the catalytic properties of binary Pd–Mn catalyst practically do not surpass those of $0.5Pd/Al_2O_3$ catalyst calcined at 1200 °C.

The data on the catalytic activity of high-temperature binary Pd–Mn catalysts where the active manganese oxide is hexaaluminate are presented in Figs. 3 and 7. One can see that the addition of just 0.5 wt.% Pd to the catalysts based on hexaaluminate $MnLaAl_{11}O_{19}$ significantly decreases the 50% methane conversion temperature (Fig. 3). The data presented in Fig. 3 show that the increase of Pd concentration in binary Pd–Mn catalysts from 0.5 to 1–2 wt.% leads to an increase of the catalytic activity. Modification of manganese hexaaluminate with 1–2 wt.% Pd leads to the decrease of the 50% methane conversion temperature from 450–465 to 360 °C at 1000 h^{-1} and from 600 to 415 °C at 24,000 h^{-1} (Fig. 7).

Thus, we have shown that the nature of the manganese oxide—Mn_3O_4, (Mn, Mg)Al_2O_4 or (Mn, Mg)$Al_{11}O_{19}$ has a significant effect on the catalytic activity of high-temperature binary Pd–Mn catalysts. An increase of the catalytic activity after palladium addition to manganese–alumina catalysts is observed only for the catalysts where the main active component is Mn_3O_4 spinel or $MnLaAl_{11}O_{19}$ hexaaluminate.

The catalytic activity data show good correlation with the TPR data. As it has been discussed above, binary Pd–Mn catalysts containing spinel-type oxide Mn_3O_4 or manganese hexaaluminate are almost completely reduced at the temperature, at which the reduction of the sample of based only on Mn compounds is just starting. In our TPR experiments the decrease of the reduction temperature of oxidic manganese species is observed even for single-component Mn catalysts after calcination at 900–1100 °C. Similar changes of the TPR profile are also observed for high-temperature Mn catalysts modified by La_2O_3 where the main active component is hexaaluminate. The shift of the TPR profile to lower temperatures suggests that supported MnO_2 and Mn_2O_3 are dispersed during the high-temperature calcination. In our opinion, the high-temperature dispersion of manganese on the alumina provides for the interaction of Mn^{3+} and/or Mn^{4+} ions with the γ-Al_2O_3 structure to form solid solutions at the stage of low-temperature manganese oxides. Calcination at 900–1100 °C leads to decomposition of the solid solutions and formation of finely dispersed particles of Mn_3O_4 spinel and α-Al_2O_3 [11,29]. According to the XRD data and earlier results [36], some Mn^{3+} cations remain in the form of a solid solution of Mn^{3+} in the alumina structure (γ-, δ-, θ-, α-Al_2O_3) [36], as indicated by the increase of γ-Al_2O_3 lattice parameter to 7.93–8.15 Å (Table 1). It should be noted that the formation of nanoscale defective Mn_3O_4 particles is believed to cause thermal activation of Mn catalysts [36].

The TPR results show that the reduction rate of oxidic manganese species grows after Pd introduction, indicating strong interaction between Pd and the Mn oxides. In addition to the reasons suggested in [14,39], the lower reduction temperature of MnO_x in the binary Pd–Mn catalysts may be due to MnO_x dispersion in the Al_2O_3 structure during the Pd deposition stage. The MnO_x dispersion may result from its partial dissolution in the impregnating solution of Pd precursor (pH ~1). This leads to an increase of the concentration of Mn^{3+} cations stabilized in the alumina structure after calcination at 500 °C. Similar to single-component Mn catalysts [18,36], calcination of binary Pd–Mn catalysts at 900 °C results in decomposition of these solid solution and formation of Mn_3O_4 nanoparticles and high-temperature forms of Al_2O_3 modified by Mn^{3+} cations. Raising the temperature over 1200 °C leads to the formation of α-Al_2O_3, manganese–alumina spinel and/or hexaaluminate doped by Mn^{3+}. It should noted that while finely dispersed particles of manganese oxides MnO_2, Mn_2O_3 and Mn_3O_4 are easily dissolved in solutions with pH ~1, manganese extraction from the structure of high-temperature

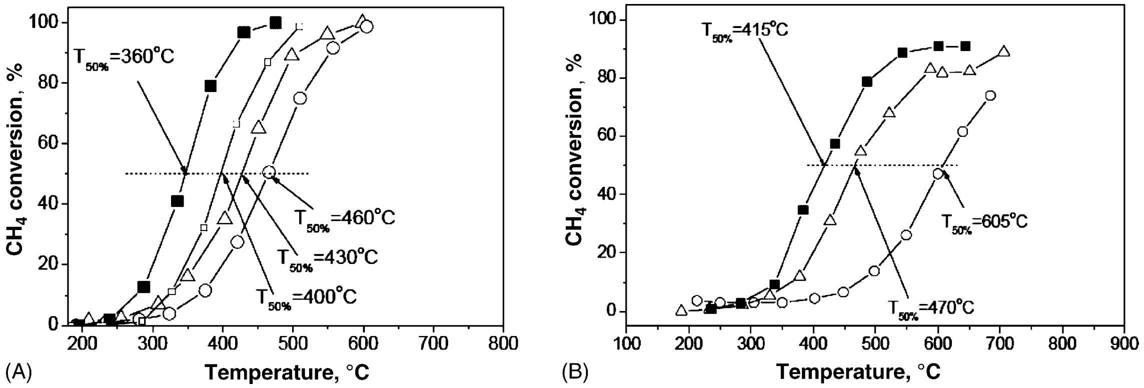

Fig. 7. Methane conversion over $3MnO_2/2.8MgO–18La_2O_3/Al_2O_3$ (○), $1.5Pd/Al_2O_3$ (△), and $1.5Pd/3MnO_2/2.8MgO–18La_2O_3/Al_2O_3$ (■) catalysts calcined at 1200 °C. A sample with Pd deposited after the formation of hexaaluminate (□) is shown for comparison. The calculated concentration of (Mg, Mn)$LaAl_{11}O_{19}$ is 100 wt.%. Test conditions: (A) 1 vol.% CH_4 in air, 1000 h^{-1}, (B) 1 vol.% CH_4 in air, 24,000 h^{-1}.

compounds, e.g. $MnAl_2O_4$ or $MnLaAl_{11}O_{19}$, is possible only at elevated temperatures. In this case, the observation of the synergetic effect in the catalytic activity of binary Pd–Mn catalysts will depend not only on the nature of the manganese oxides, but also on the catalyst preparation procedure.

To check this hypothesis, we studied the catalytic activity of binary Pd–Mn samples modified with Pd after the formation of spinel (Table 3, no. 5) or hexaaluminate (Fig. 7A; Table 3, no. 4) phases. After the addition of 0.5 wt.% Pd in $5MnO_2/Al_2O_3$ catalyst calcined at 1200 °C and containing manganese–alumina spinel, $T_{50\%\,CH_4}$ was 480 °C, which is higher than for $0.5Pd/Al_2O_3$ catalyst (Fig. 3, 430 °C). The deposition of 0.5 wt.% Pd on the high-temperature sample containing the manganese hexaaluminate phase leads to an increase of the catalytic activity of the initial catalyst. However, the activity growth was much weaker than for modification of the low-temperature hexaaluminate precursors followed by the formation of hexaaluminate phase at 1200 °C. $T_{50\%\,CH_4}$ was 400 °C, which is lower by 60 °C than for the initial Mn–Al catalyst and by 30 °C than for $0.5Pd/Al_2O_3$. Indeed, the synergetic effect of Pd and manganese oxides is observed only if palladium is introduced at stage of the low-temperature precursor of the manganese–alumina spinel or manganese hexaaluminate. The synergetic effect is not observed when high-temperature samples with formed spinel or hexaaluminate phases are modified with Pd.

4. Conclusions

The possibility of stabilization of various oxidic manganese species by variation of the loadings of MnO_2 (3–11 wt.%), La_2O_3 (5–21 wt.%) and MgO (2–3 wt.%) in catalysts prepared on granulated $(\gamma + \chi)$-Al_2O_3 at calcination temperatures 900 and 1200 °C is demonstrated.

A strong synergetic effect in the catalytic activity in methane oxidation has been observed after introduction of 0.5–2 wt.% Pd to manganese–alumina catalysts stabilized in the form of Mn_3O_4 spinel doped with Al^{3+} cations or as hexaaluminate (Mn, Mg)$LaAl_{11}O_{19}$.

The synergetic effect of palladium and Mn_3O_4 or $MnLaAl_{11}O_{19}$ provides a low light-off temperature and high efficiency of the catalyst at high temperatures. The formation of high-temperature hexaaluminates $MnLaAl_{11}O_{19}$ and (Mn, Mg)$LaAl_{11}O_{19}$ improves the thermal stability of the catalyst, making it possible to increase the operation temperature of Pd catalysts up to 1000–1200 °C.

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