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Effect of Preliminary Mechanical Treatment of the Reaction Mixture on Properties of Sr₂TiO₄-Based Catalysts*

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Abstract

The paper explores conditions effect of mechanochemical activation (different initial components and various activation times) on the phase and surface composition, texture characteristics of strontium titanate-based catalysts with the layered perovskite structure and their activity in the reaction of the oxidative coupling of methane (OCM) at temperatures of 800–900 °C. The resulting catalysts were characterized by XRD, mercury porosimetry, BET, SEM, and XPS. Conditions for preparation of single-phase well-crystallized Sr₂TiO₄, such as the use of a mixture of TiO₂ and SrCO₃ as initial components, the activation time of 8 min, and calcination at 1100 °C for 4 h were selected. It was demonstrated that catalysts obtained using the mechanochemical method had higher activities in the OCM reaction (higher methane conversion and C₂ hydrocarbon yields) compared to those produced by the co-precipitation method.

Keywords: layered perovskite-like oxides, mechanochemical synthesis method, oxidative coupling of methane

INTRODUCTION

Layered perovskite-like oxides have unique physical and chemical properties (high-temperature superconductivity, high ion conductivity, and high magnetoresistance, and also catalytic and photocatalytic activity) [1]. Their structure is alternating layers of perovskite and metal oxide having a cubic lattice of the NaCl type, which allows wildly varying the composition of such compounds and thereby have an effect on their physical properties, electronic structure, and catalytic activity.

It was recently demonstrated that strontium titanate compounds with a layered structure of perovskite (Sr₂TiO₄) might act as catalysts for the oxidative coupling of methane (OCM) [2] ensuring 12–14 % yields of ethane and ethylene at 850–900 °C with methane conversion of about 20 % and a selectivity to C₂ hydrocarbons of 60–68 %. This reaction is of practical relevance, as it allows producing natural gas-derived ethylene that is one of the demanded compounds in the chemical industry [3].

High-temperature solid-phase synthesis involving preparation of a stoichiometric mixture of initial oxides followed by annealing at $T = 1200\text{--}1400$ °C for 10–15 h is traditionally used to synthesise Sr₂TiO₄ [4]. This procedure is characterised by long duration and the requirement to

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carry out processes at high temperatures. Other methods, such as co-precipitation, sol-gel deposition, and the citrate technique, are notable for the multi-step nature, the need to use specially prepared solutions, and also as by possible contamination of synthesis products [5]. Mechanochemical activation (MA) of the initial reagents allows softening the conditions for the production of ceramic materials and having an effect on their physical and chemical properties [6].

This research explores the effect of conditions of mechanical activation (different initial reagents and activation duration) on the phase composition, texture, the surface morphology of perovskite-like catalysts of the Sr_2TiO_4 composition, and their activity in the OCM reaction. Properties of catalysts produced by the mechanochemical method and co-precipitation technique were compared.

EXPERIMENTAL

Initial materials for synthesis were TiO_2 , SrCO_3 , and SrO , produced by the decomposition of $\text{Sr}(\text{NO}_3)_2$ (all being of chemical pure grade) at $800\text{ }^\circ\text{C}$ for 4 h. Activation of the initial reagents taken in the stoichiometric ratio was carried out in a planetary mill APF-5 with a power of 0.37 kW at a rotation speed of the planetary disk of 850 rpm and 40g acceleration. The ratio of the grinding balls mass to the activated loading was 4 : 1; the loading mass and the grinding time were 30 g and 4–8 min, respectively. All the resulting samples were calcined at $1100\text{ }^\circ\text{C}$ for 4 h. Strontium oxide or carbonate-derived specimens after mechanical activation for 4 and 8 minutes are further designated as MO4/MO8 and MC4/MC8, respectively.

A reference material (RM) was produced by co-precipitation technique from a combined solution of H_2TiCl_6 and $\text{Sr}(\text{NO}_3)_2$ in the stoichiometric ratio of cations. A 0.5M solution of K_2CO_3 was used as a precipitator. Precipitation was carried out at room temperature until a pH of 9.5. Afterwards, the precipitate was filtered off, washed until a pH of 7 and dried for 10 h at $120\text{ }^\circ\text{C}$ followed by calcination at $1100\text{ }^\circ\text{C}$ for 4 h [5].

X-ray phase analysis was performed using the Bruker D8 X-ray diffractometer (Germany) using CuK_α radiation ($\lambda = 1.5418\text{ \AA}$) when scanning at points with an interval of 0.05° in a range of 2θ from 20 to 70° . Phase composition identification was carried out using JCPDS (PC version of PDF for Windows 2000).

Catalysts porous structure was determined by mercury porosimetry using the AutoPore 9200 device. Specific surface area (S_{sp} , m^2/g) of samples was determined according to the thermal desorption of argon.

The XPS spectra were recorded using the SPECS spectrometer (Germany) equipped with the PHOIBOS-150-MCD-9 analyser using non-monochromatic MgK_α irradiation ($h\nu = 1253.6\text{ eV}$) at 200 W. In order to correctly calibrate photoelectron lines, the internal standard method was used (the C1s line of 284.5 eV binding energy). Surface concentrations of Ti, Sr, O were calculated based on photoelectron peak intensities considering atomic sensitivity coefficients. Decomposition of spectra was carried out in the XPS PEAK-4.1 software using the Gauss-Lorentz function. Background subtraction was performed by the Shirley method.

Catalytic activity in the OCM reaction was determined in flow type setup at the ambient pressure and a temperature of $750\text{--}900\text{ }^\circ\text{C}$. Samples were tested as a fraction of 0.25–0.5 mm, 20 mg of catalyst sample being used. The feed rate of the reaction mixture (45 % of CH_4 + 11 % of O_2 in nitrogen gas) was 30 L/h, which corresponded to a contact time of 0.024 s. Analysis of the initial reaction mixture and reaction products was carried out using sequentially coupled LXM-80 and Tsvet-500 gas chromatographs. Helium was used as a carrier gas. Gases, such as CO_2 and C_2 hydrocarbons, were separated in a column with HayeSep C polymer sorbent ($2\text{ m} \times 3\text{ mm}$), while H_2 , O_2 , N_2 , CH_4 , and CO in a column with 5A zeolite ($3\text{ m} \times 3\text{ mm}$) at temperatures of 60 and $90\text{ }^\circ\text{C}$, respectively.

RESULTS AND DISCUSSION

Phase composition

Figure 1 gives X-ray analysis data for all produced samples during activation of the initial components for 4 and 8 min, and also the reference material (RM) after calcination at $1100\text{ }^\circ\text{C}$.

Table 1 presents phase composition data, the calculated parameters of the unit cell with the Sr_2TiO_4 structure, and the average crystallite size.

As demonstrated in [5], when the co-precipitation technique is used, pure Sr_2TiO_4 with the layered perovskite structure (space group $I4/mmm$) is formed. The sample is well-crystallized; its particles sizes are $\sim 550\text{ \AA}$. Lattice parameters are close to the literature data [7].

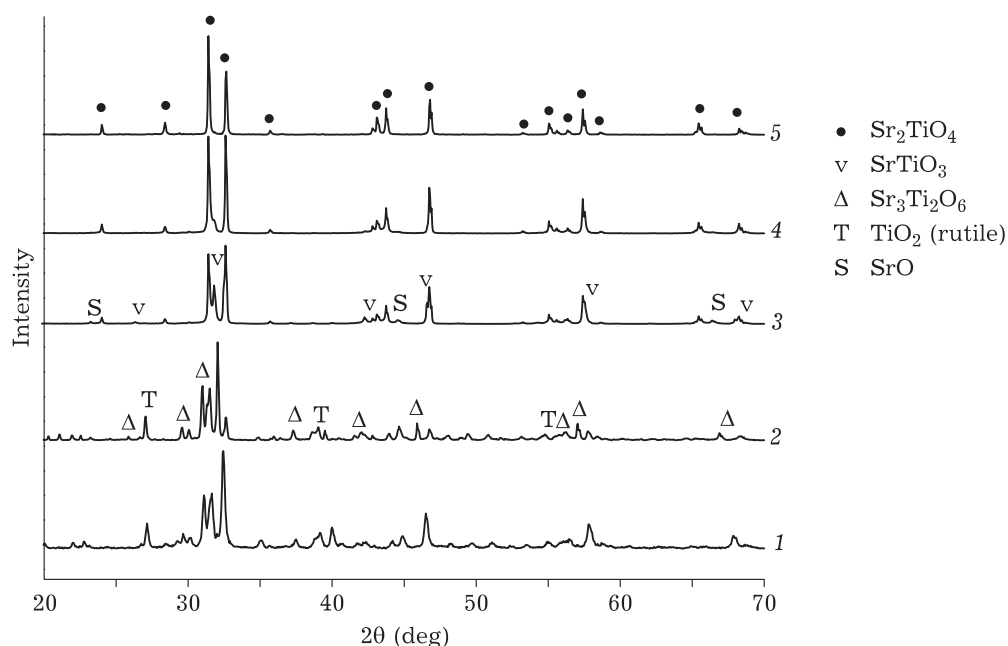


Fig. 1. X-ray diffraction patterns of samples MO4 (1), MC4 (2), MO3 (3), MC8 (4), and RM (5) after calcination at 1100 °C.

According to [8], there is no layered perovskite phase formation when TiO₂ and SrCO₃ are mixed even during calcination at 1200 °C [8]. After calcination of samples obtained by 4 min mechanical activation of the initial mixtures with both oxide (sample MO4) and with strontium carbonate (sample MC4), the X-ray diffraction patterns also contain lines corresponding to the formation of various Ruddlesden-Popper phases (SrTiO₃, Sr₂TiO₄,

Sr₃Ti₂O₇), and also peaks of the initial components (TiO₂ and SrO, see Fig. 1). The formation of a multicomponent system with the prevalence of the layered perovskite phase was also noted in [2] during the activation of a mixture of TiO₂ and SrCO₃ for 3 min. Apparently, a longer, or more intense exposure on the initial components is required for the formation of single-phase oxide, as demonstrated in [8]. Calcination of a mixture TiO₂

TABLE 1

Phase composition, Sr₂TiO₄ unit cell parameters, crystallite size, specific surface area (S_{BET}), total pore volume (V_{pore}) and median pore diameter (D_{pore}) of the resulting samples

Sample	Phase composition	Cell parameters, Å		CSR, Å	S_{BET} , m ² /g	V_{pore} , cm ³ /g	D_{pore} , μm
		$a = b$	c				
MO4	Sr ₃ Ti ₂ O ₇ Sr ₂ TiO ₄ SrTiO ₃ TiO ₂ , SrO	n/d	n/d	–	2.3	0.23	0.11
MC4	Sr ₃ Ti ₂ O ₇ Sr ₂ TiO ₄ SrTiO ₃ TiO ₂ , SrO	n/d	n/d	–	1.6	0.27	0.76
MO8	Sr ₂ TiO ₄ SrTiO ₃ Traces SrO	3.891(5)	12.500(0)	470	1.6	0.34	0.61
MC8	Sr ₂ TiO ₄	3.883(2)	12.566(9)	540	1.0	0.17	0.51
RS	Sr ₂ TiO ₄	3.888(6)	12.601(4)	550	0.8	0.11	0.86

Note. n/d – not determined.

and SrCO_3 activated in the planetary mill (Fritsch Pulverisette 7 at a rotational frequency of a planetary disk of 400 rpm and the 10 : 1 mass ratio of the grinding balls to the activated load for 110 h) yielded single-phase SrTiO_4 .

Indeed, there is reducing the content of impurity phases when enhancing the activation time of the initial components until 8 min. Nevertheless, the sample produced by activation of a mixture of TiO_2 and SrO (MO8) remains mixed-phase and comprises of mixed phases of Sr_2TiO_4 and SrTiO_3 , whereas the use of strontium carbonate (sample MC8) leads to single-phase Sr_2TiO_4 . The observed discrepancies in lattice parameters for samples MO8/MC8 and the sample obtained by the co-precipitation technique may be due to various irregularities therein.

Texture characteristics

Table 1 gives the data of the specific surface area, the total pore volume, and the median pore diameter of the resulting samples. Samples produced by calcination of the initial components after mechanical activation for 4 min are characterised by higher specific surface area (1.6–2.3 m^2/g) probably due to the mixed-phase composition, especially in case of the use of strontium oxide as the initial component. When increasing the time of mechanical activation leading to the formation of single-phase samples of strontium titanate, there is a lower specific surface area of 1.0–1.6 m^2/g . For single-phase Sr_2TiO_4 obtained by co-precipitation technique, $S_{\text{sp}} = 0.8 \text{ m}^2/\text{g}$.

Figure 2 presents SEM data for Sr_2TiO_4 synthesized in different methods: after mechanical activation for 8 min (MO8 и MC8) and RS. It was found that the strontium oxide-derived sample represented 0.5–1.0 μm irregularly shaped Sr_2TiO_4 particles bound into larger agglomerates. The presence of individual smaller particles of strontium titanate (SrTiO_3) is also possible. When strontium carbonate is used as the initial component, larger round-shaped 3 μm particles are formed. The RS is also characterised by similar well-sintered round-shaped particles with an average size of over 5 μm . It is worth noting that Sr_2TiO_4 crystallite sizes determined by XRD are much lower than SEM data, which testifies the microblock structure of particles observed by SEM.

Apparently, the observed particles are non-porous, as the median pore diameter for different samples is 0.11–0.86 μm and is comparable with particle sizes (see Table 1). In this manner, one may assume that the porous structure of samples is formed by pores between particles with a size up to 3 μm and the specific surface area of the specimens is defined by the geometric surface of these species. This explains the higher specific surface area of MO samples characterized by the presence of smaller particles compared to the MC sample.

Surface composition

In order to explore the surface composition of the resulting samples, the XPS method was used. A symmetrical Ti 3p peak was observed for all samples at 457.4–457.5 eV corresponding to Ti^{4+}

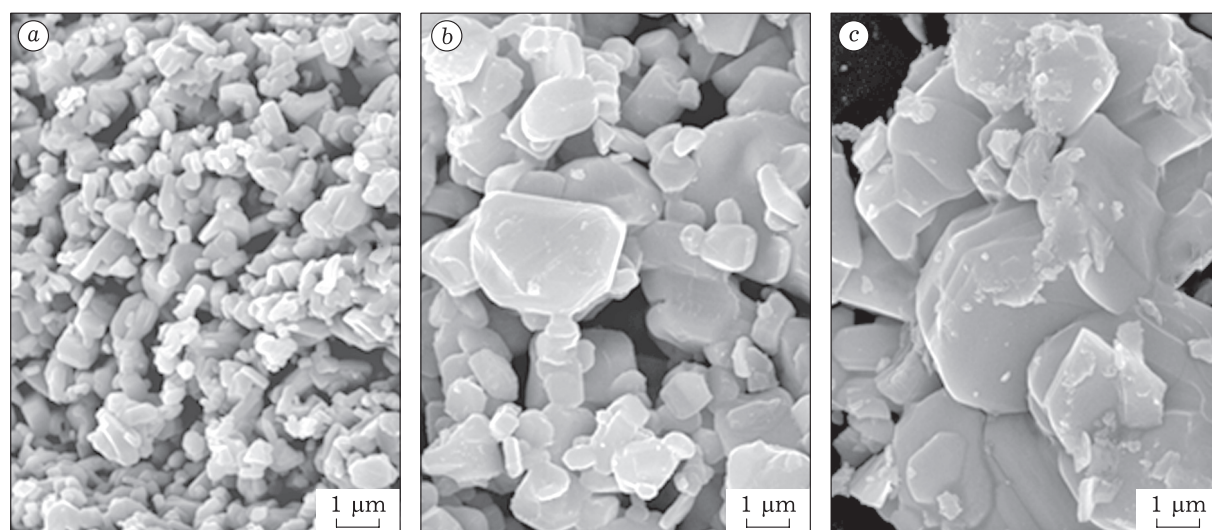


Fig. 2. SEM data for the prepared samples of Sr_2TiO_4 MO8 (a), MC8 (b) and the reference material (c).

in perovskite. In the spectrum of Sr, there are two $3d_{5/2}$ peaks corresponding to Sr²⁺ in the composition of oxide (132.2–132.3 eV) and perovskite (132.7–132.8 eV) [9]. As the position of these peaks is very close, it is difficult to determine correctly the amount of strontium in different states. There are three overlapping peaks with binding energies of 528.5–528.8, 530.6–531.2, and 533.0–533.6 eV in O1s photoelectron spectra of the samples. The first and second peaks correspond to O²⁻ in the structure of perovskite (O_{per}) or strontium oxide (O_{ox}), respectively. The third peak may be referred to oxygen in the composition of surface hydroxides [10].

Proceeding from XPS data, surface concentrations for titanium and strontium ions, different oxygen forms, and also their ratio were computed (Table 2). As demonstrated by the findings, on the surface of the sample produced by the co-precipitation method, the Sr/Ti ratio is much higher than the stoichiometric value for layered perovskite Sr₂TiO₄. The surface of this sample is likely to be enriched with strontium compounds, which is a peculiarity of this preparation method [5]. Samples obtained by the mechanochemical method have the Sr/Ti ratio close to 2, which testifies a more uniform distribution of perovskite SrTiO₃ and strontium oxide layers on the surface. However, the O_{ox}/O_{per} ratio is less than 1, which points to a predominance of perovskite layers, especially for samples obtained by mechanical activation for 4 min.

Catalytic activity

Table 2 gives data regarding the activity of the catalysts produced in the OCM reaction, such as methane conversion degree, selectivities and yields of C₂ hydrocarbons (ethane and ethylene), and also reaction product ratios at catalyst bed temperature of 900 °C. Samples MO4 and MO8 produced from strontium oxide and characterised by the higher specific surface area and the presence

of SrTiO₃ on the surface (according to XPS data) show the highest methane conversion. Strontium-enriched single-phase sample (RM) with the low specific surface area produced by co-precipitation method showed the lowest methane conversion.

As it follows from the findings, multiphase samples have lower selectivity to C₂ hydrocarbons, which may be related to the presence of weakly bound oxygen in the interphase boundaries. It facilitates the occurrence of methane combustion reaction [11]. A significant prevalence of CO₂ in reaction products over MO4 and MC4 catalysts also proves this. Single-phase samples MC8 and RM show the highest selectivity to C₂ hydrocarbons, however, the difference in the surface composition of these catalysts have an effect on the ratio of reaction products. The catalyst produced by mechanical activation shows higher selectivity to ethylene. The maximum yield of C₂ hydrocarbons was 10–12 %, when catalysts prepared by mechanical activation from a mixture of TiO₂ and SrO, the surface of which was depleted in strontium, were used.

CONCLUSION

Strontium titanate-based catalysts with the layered perovskite structure of Sr₂TiO₄ were produced in the research by the mechanochemical method in a planetary mill using different initial components (TiO₂ and SrO or SrCO₃) and activation times (4 or 8 min). It was demonstrated that short-term activation of initial components after thermal treatment at 1100 °C resulted in the formation of a multiphase system characterized by the presence of small particles, high specific surface area, and methane conversion degree to predominantly form CO₂. It was determined that with increased activation time, almost single-phase Sr₂TiO₄ with larger particles, low specific surface area, and higher selectivity to C₂ hydrocarbons was formed in the reaction of the oxida-

TABLE 2
XPS data for prepared samples and their catalytic activity (methane conversion degree, C₂ selectivity and hydrocarbon yields) in OCM reaction at 900 °C

Sample	XPS data				Activity in OCB				
	O _{ox} /T	O _{per} /Ti	O _{ox} /O _{per}	Sr/Ti	X(CH ₄)	S(C ₂), %	Y(C ₂), %	CO/CO ₂	C ₂ H ₆ /C ₂ H ₄
MO4	1.62	3.28	0.49	1.62	22.3	49.0	10.9	0.18	1.04
MC4	2.18	3.64	0.60	2.36	16.0	55.8	8.9	0.17	0.77
MO8	2.56	3.40	0.75	1.97	19.8	59.6	11.8	0.42	0.54
MC8	2.39	3.46	0.69	2.09	13.6	62.5	8.7	0.73	0.58
RS	22.73	3.14	7.24	7.56	8.0	64.2	5.1	0.84	1.90

tive coupling of methane (OCM). Herewith, it is preferable to use strontium carbonate instead of oxide as an initial component. The XRD and XPS investigation of Sr_2TiO_4 samples produced by the mechanochemical method and co-precipitation method detected a major difference in their phase and surface compositions. It was determined that the mechanochemical method with a number of advantages, such as simplicity, reliability, and a lack of pernicious drains, made it possible to produce a catalyst that ensured almost a twice higher yield of C_2 hydrocarbons in the OCM reaction compared to that produced by co-precipitation technique.

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