

Catalytic Properties of SnO_2 – TiO_2 Compositions in Total Methane Oxidation

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Abstract—Tin and titanium dioxides and their compositions were studied as catalysts for the reaction of complete oxidation of methane. The catalytic activity of the test samples was compared in terms of first-order reaction rate constants with reference to the unit surface area of a catalyst. The crystal structures and specific surface areas of the obtained compositions were characterized. The thermal stability of SnO_2 was investigated. Data on the temperature-programmed reduction of SnO_2 and the composition $\text{Sn}_{0.70}\text{Ti}_{0.30}\text{O}_2$ in hydrogen were given.

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INTRODUCTION

A serious environmental problem is connected with the neutralization of methane, whose concentrations in exit gases is lower than 4 vol %. In particular, this problem appears in the development of systems for the afterburning of methane, which is present in the vent gases of coal mines. Its solution will make it possible to exclude the release of CH_4 , whose negative effect as a greenhouse gas is greater than the effect of CO_2 by a factor of 21, into the atmosphere. Technically, catalytic combustion is the most reasonable process for solving this problem [1].

The catalytic combustion of methane is currently performed on expensive and thermally unstable supported Pd catalysts. Oxide compositions with the structure of perovskite could become a potential alternative to palladium catalysts. However, they, as well as Pd catalysts, are unstable to catalytic poisons, namely, sulfur dioxide, the presence of which in exit gases is explained by the oxidation of sulfur-containing components, which are the constituents of the absolute majority of fuel mixtures.

Alifanti [2] and Arosio et al. [3] found that the irreversible poisoning of oxide catalysts is caused by the formation of sulfates, which block the active surface. On this basis, it is possible to conclude that only two categories of metal oxides can be resistant to sulfur-containing gas impurities. Namely, these are either metal oxides that do not react with sulfur oxides at elevated temperatures (this is highly improbable) or metal oxides that form thermally unstable sulfates, which decompose at elevated temperatures (500–800°C) to form oxides possessing practically acceptable catalytic activity. An analysis of published data [4,

5] showed that TiO_2 and SnO_2 can be of interest with respect to the thermal instability of sulfates; these are refractory compounds, which crystallize in related structures. Data on the catalytic activity of these compounds in the reaction of methane oxidation are scanty. We failed to find the sources of reliable information on this subject matter for titanium(IV) oxide and its solid solutions with tin oxide. The behavior of tin(IV) oxide was described elsewhere [6, 7].

The aim of this work was to obtain information on the catalytic activity of SnO_2 , TiO_2 , and SnO_2 – TiO_2 compositions in order to determine the applicability of these materials as catalysts for methane oxidation and, if appropriate, to study the behavior of the most active catalysts in the oxidation of methane in the presence of sulfur dioxide. In this work, we also studied the physicochemical and catalytic properties of tin(IV) oxide, titanium(IV) oxide, and SnO_2 – TiO_2 compositions, in which solid solutions can be formed, as judged from structural data and unit cell parameters.

EXPERIMENTAL

Synthesis of Tin and Titanium Oxides and Their Solid Solutions

Tin(IV) oxide was synthesized by precipitation of Sn(II) hydroxide from tin(II) chloride followed by decomposition and oxidation on heating in air. Aqueous solutions of ammonia or oxalic acid were used as precipitating agents. The resulting hydroxide and oxalate precipitates were centrifuged and thoroughly washed with water. Thereafter, the samples were dried at 90–110°C and then calcined in a muffle furnace; the temperature was increased to 700°C at a rate of

Specific surface areas (S_{sp}) of the synthesized samples

Sample	ΔS_{sp} (BET), m^2/g
TiO_2 ($\text{C}_2\text{H}_2\text{O}_4 + \text{NH}_4\text{OH}$)	2.8
$\text{Sn}_{0.15}\text{Ti}_{0.85}\text{O}_2$	18.5
$\text{Sn}_{0.30}\text{Ti}_{0.70}\text{O}_2$	27.8
$\text{Sn}_{0.50}\text{Ti}_{0.50}\text{O}_2$	21.4
$\text{Sn}_{0.70}\text{Ti}_{0.30}\text{O}_2$	18.2
$\text{Sn}_{0.85}\text{Ti}_{0.15}\text{O}_2$	16.1
SnO_2 (NH_4OH)	9.0
SnO_2 ($\text{C}_2\text{H}_2\text{O}_4$)	13.1

2 K/min, and the samples were kept at this temperature for 3 h.

Titanium dioxide was synthesized by dissolution of titanium *tert*-butoxide $\text{Ti}(\text{OC}_4\text{H}_9)_4$ in an aqueous solution of oxalic acid followed by precipitation with an aqueous solution of ammonia. The resulting precipitate was centrifuged and thoroughly washed with water. Then, it was dried and calcined analogously to the other samples.

The $\text{Sn}_x\text{Ti}_{1-x}\text{O}_2$ solid solutions (where $x = 0.15, 0.30, 0.50, 0.70$, and 0.85) were synthesized by coprecipitation of tin and titanium hydroxides from a solution prepared by mixing the solutions of tin chloride and titanium butoxide dissolved in oxalic acid. An aqueous solution of ammonia was used as a precipitating agent. The resulting precipitates were centrifuged and washed with water. Then the samples were dried and calcined under the same conditions as in the case of individual oxides.

Catalyst Characterization

X-ray diffraction (XRD) analysis was performed on a DRON-3M diffractometer (CuK_α radiation; Ni filter; $\lambda = 0.15418$ nm) in the range of 2θ angles from 10° to 80° . The experimental diffraction patterns were compared with the JCPDS database (Joint Committee on Powder Diffraction Standards).

The specific surface areas of the samples were measured by the thermal desorption of nitrogen. The table summarizes the specific surface areas of the test samples.

Determination of Catalytic Activity

The catalytic activity of the prepared samples in the reaction of complete methane oxidation was investigated using a setup whose construction and operating

conditions were described elsewhere [8]. It consisted of the following three main blocks: a gas pipeline, a flow quartz reactor, and an INFRALIGHT 11P IR analyzer of reaction products. A quartz grid covered with quartz wool, on which a catalyst mixed with a quartz filler in a ratio of 1 : 6 (200 mg of a catalyst per 1.2 g of quartz powder with a particle size of 0.3–0.5 mm) was placed, was arranged in the middle part of the tubular reactor with an inside diameter of 10 mm and a length of 450 mm. The average particle size of the catalyst was 1.0 μm , and it was not additionally fractionated in the course of experiments.

A mixture of methane with artificial air ($\text{N}_2 : \text{O}_2 = 1 : 5$) with a methane concentration of 1% was used in the oxidation of methane. The total flow rate of the gas mixture was 75 ml/min. The experiments were performed over the temperature range of 350–700°C. The limits of detection were 0.01, 0.001, and 0.01% for methane, CO, and CO_2 , respectively. Carbon monoxide was not detected in the reaction products within the limits of gas analyzer sensitivity.

The reaction rate constant per unit specific surface area was chosen as a value for comparing the activities of the catalysts in the reaction of complete methane oxidation. An equation for calculating the rate constant, on the basis of a first-order reaction with respect to methane, has the following form:

$$k_s = \ln\left(\frac{1}{1-\alpha}\right) \frac{F}{PmS_{sp}} \left[\mu\text{mol s}^{-1} \text{ m}^{-2} \text{ atm}^{-1} \right], \quad (1)$$

where F is the total gas flow rate [$\mu\text{mol/s}$]; S_{sp} is the specific surface area [m^2/g]; P is the total pressure in the system [atm]; α is the conversion; and m is the catalyst weight [g].

The conversion of methane (α) was calculated based on the methane content of the gas mixture at the reactor outlet using the equation

$$\alpha = \frac{C_{\text{CH}_4}^0 - C_{\text{CH}_4}}{C_{\text{CH}_4}^0} = \frac{P_{\text{CH}_4}^0 - P_{\text{CH}_4}}{P_{\text{CH}_4}^0}, \quad (2)$$

where $C_{\text{CH}_4}^0 (P_{\text{CH}_4}^0)$ is the initial concentration (partial pressure) of methane, and $C_{\text{CH}_4} (P_{\text{CH}_4})$ is the current concentration (partial pressure) of methane.

Temperature-Programmed Reduction (TPR) of Samples in Hydrogen

The reduction of samples was studied in a batch mode using a circulation absorption system with the absorption of water, whose diagram was published previously [9]. A ceramic container with a 0.5-g oxide

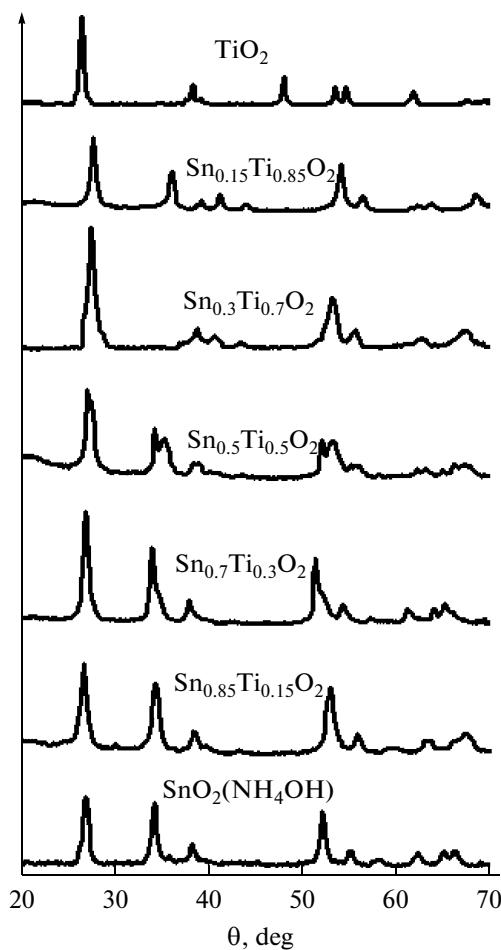


Fig. 1. X-ray diffraction patterns of TiO_2 , SnO_2 , and their compositions.

sample was loaded into the reactor; air was pumped out from the system, and hydrogen was added to a specified pressure. Changes in the pressure of H_2 were measured with the use of a deformation membrane sensor from Vernier (United States). Next, the reactor with the container was placed in a furnace, and a compressor was turned on to provide gas circulation. The temperature was increased at a rate of 3–6 K/min (in a range from 100 to 750°C), and changes in the pressure of hydrogen were measured in the course of the experiment.

RESULTS AND DISCUSSION

The X-ray diffraction patterns shown in Fig. 1 demonstrate that tin dioxide has the structure of rutile and titanium dioxide has the structure of anatase. The introduction of 15% tin dioxide into TiO_2 led to the stabilization of the structure of rutile, and it was accompanied by changes in the lattice parameters of the titanium dioxide phase. Note that the width of diffraction peaks in the X-ray diffraction patterns notice-

ably increased, and this was supported by an increase in the specific surface areas of the samples upon the introduction of SnO_2 . An increase in the tin dioxide content to 30% led to a further shift of diffraction peaks.

The X-ray diffraction pattern of the sample containing 50% SnO_2 was dramatically different from those of the samples with 15 and 30% SnO_2 ; this difference indicates the formation of a two-phase system. One system of peaks characterizes a solid solution on the basis of titanium dioxide with the modification of rutile, whereas the other belongs to a solid solution of tin dioxide with the structure of rutile.

At SnO_2 concentrations up to 70%, signs of heterogeneity were retained, whereas the solutions can be considered homogeneous at 85% SnO_2 , and they did not exhibit peaks other than those due to a solid solution of tin dioxide.

Thus, the results of structural analysis showed that compositions in the SnO_2 – TiO_2 series form limited solid solutions on the basis of titanium dioxide (to 30% SnO_2) and on the basis of tin dioxide (to 85% SnO_2).

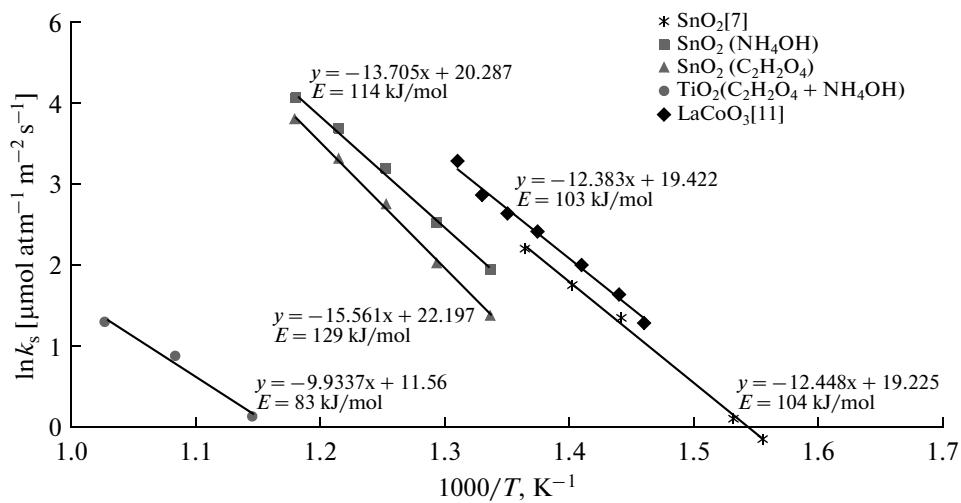


Fig. 2. The temperature dependence of the rate constants of total CH_4 oxidation on SnO_2 , TiO_2 , and LaCoO_3 .

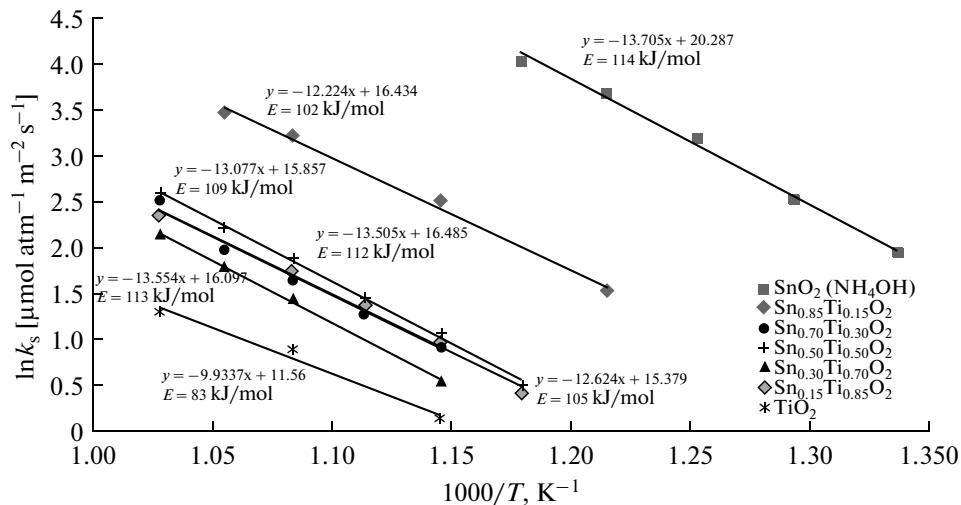


Fig. 3. The temperature dependence of the rate constants of total CH_4 oxidation on SnO_2 – TiO_2 compositions.

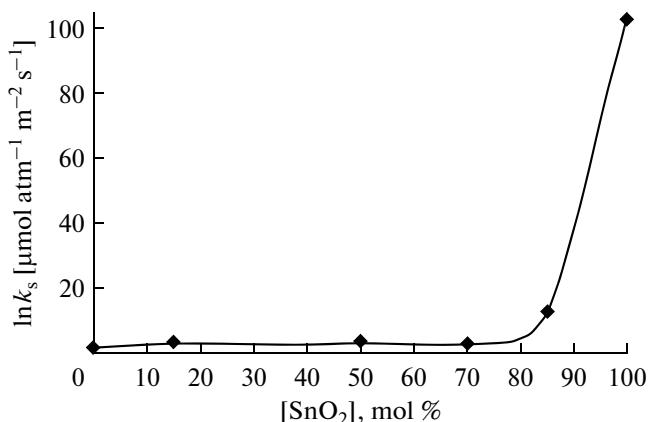


Fig. 4. Dependence of the reaction rate constant on the concentration of SnO_2 ($T = 600^\circ\text{C}$).

In the range of 40–80% tin dioxide, the system is inhomogeneous and contains two phases with different relative concentrations of either of them.

Figure 2 characterizes the catalytic activity of tin dioxide and titanium dioxide and also published data for SnO_2 [7] in the Arrhenius coordinates. The prepared samples of tin dioxide had catalytic activity comparable with published data [7], but it was somewhat lower and characterized by a higher activation energy. Titanium dioxide exhibited extremely low catalytic activity: the conversion of methane even at 700°C was only 11%. The linearity of the temperature dependence of the rate constant in the $\ln k_s$ – $1/T$ coordinates confirms the correctness of the value chosen for processing experimental data.

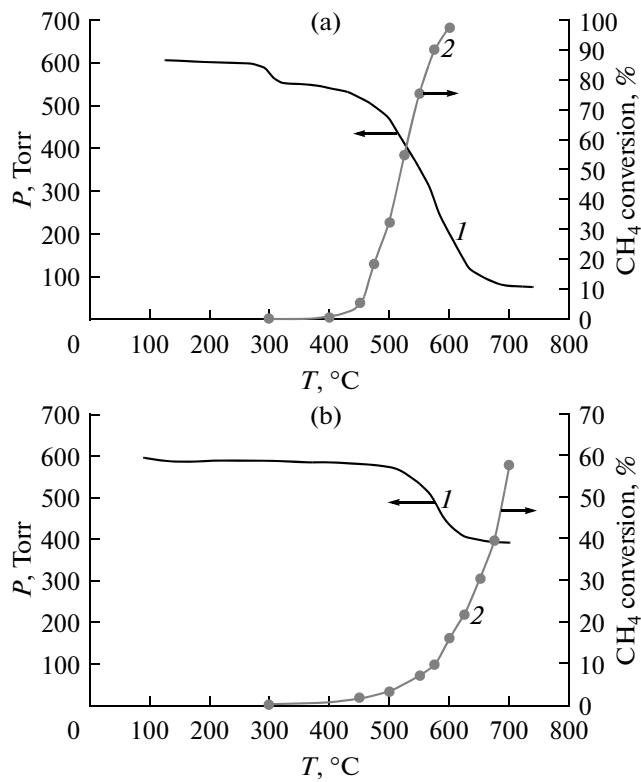


Fig. 5. Comparison between the temperature dependence of (2) the catalytic activity of (a) SnO_2 or (b) $\text{Sn}_{0.70}\text{Ti}_{0.30}\text{O}_2$ and (1) the reduction of the samples in hydrogen.

Figures 3 and 4 show data on the catalytic activity of SnO_2 – TiO_2 compositions depending on catalyst composition. As can be seen, the introduction of only 15% TiO_2 leads to a decrease in the catalytic activity by a factor of 8, and a further increase in the concentration of TiO_2 leads to a decrease to the values close to the activity of pure TiO_2 .

The observed effect suggests a pronounced inhibiting effect of TiO_2 . According to published data, the catalytic activity of the oxides of metals that occur in different charge states is related to the redox mechanism of catalysis [5]. It is well known that the higher oxide of tin contains tin ions of different valence, including ions with a charge of 2+, the presence of which is responsible for the electrical properties of this oxide [10]. It is believed that the introduction of TiO_2 stabilizes the charge state Sn^{4+} and, as a result, decreases the catalytic activity of the phase of $\text{SnO}_{2-\delta}$. To test this hypothesis, we investigated the curves of the temperature-programmed reduction (TPR) of SnO_2 and its $\text{Sn}_{0.70}\text{Ti}_{0.30}\text{O}_2$ composition in hydrogen.

Figure 5 shows the results of these experiments and compares them with the temperature dependence of the conversion of methane. As is evident, the reduction of pure tin dioxide occurs in two steps: (1) the reduction of SnO_2 to SnO and (2) the reduction of SnO to Sn . On the contrary, the reduction of the mixed

composition $\text{Sn}_{0.70}\text{Ti}_{0.30}\text{O}_2$ in an atmosphere of hydrogen occurs at a single step (SnO_2 is reduced to Sn), which is strongly shifted to the high-temperature region. A comparison of the temperature dependence of the conversion of methane upon oxidation (curve 2) with TPR data (curve 1) reveals a correlation between the reduction of the catalyst and its catalytic activity. Thus, these experiments confirmed the hypothesis

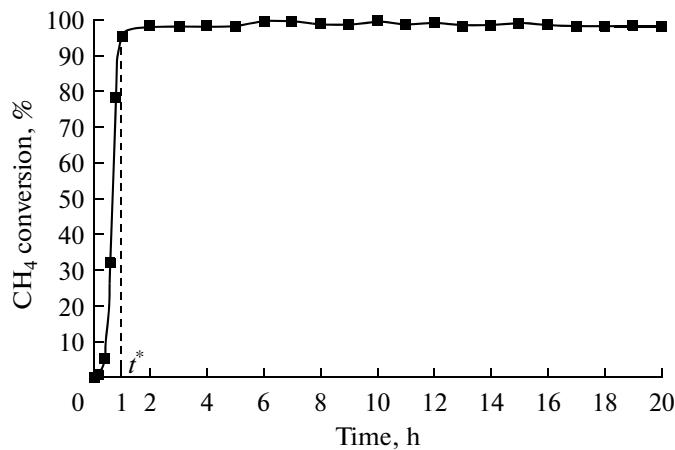


Fig. 6. Thermal stability of SnO_2 (t^* is the time taken to reach a conversion of $\geq 90\%$).

that a sharp decrease in the catalytic activity of a solid solution on the basis of SnO_2 upon the introduction of TiO_2 is caused by the stabilization of tin in a charge state of 4+.

It was also of interest to compare the catalytic properties of tin dioxide and LaCoO_3 , which is the most active among perovskite catalysts [11]. As can be seen in Fig. 2, the catalytic activity of tin dioxide is fully comparable with that of lanthanum cobaltite.

Because tin dioxide was found most active among all of the catalysts tested in this work, we obtained data on the stability of catalytic action for a long time interval at temperatures when the conversion of methane was higher than 90%. The experiments were conducted as follows: heating to 700°C followed by a 20-h-long exposure at this temperature to a flow of the reaction gas mixture. Figure 6 shows that the reaction atmosphere did not lead to a change in the catalyst activity (98.7% conversion) in the specified time interval under extreme temperature conditions of catalyst operation. The experiments carried out simultaneously showed that the surface area of SnO_2 remained unchanged upon the thermal treatment of the oxide at 700°C with 6- to 15-h exposures.

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