Mesoporous nanostructured $Ti_xSn_{1-x}O_4$ mixed oxides as catalysts for methanol decomposition: effect of Ti/Sn ratio

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The aim of the current investigation is to elucidate the impact of the Ti/Sn ratio in $Ti_xSn_{1-x}O_4$ mixed oxides on their textural, structural, redox, and catalytic features. Mesoporous mixed oxides of different Ti/Sn ratio were synthesised by template-assisted hydrothermal technique. The obtained materials were characterised by a complex of physicochemical techniques, such as nitrogen physisorption, XRD, Raman, UV–Vis, FTIR, and TPR with hydrogen. Methanol decomposition to syngas was used as a test reaction. The catalytic activity of the binary materials was affected in a complicated way by their phase composition. The latter was improved due to an increase in material specific surface area and pore volume and strongly suppressed because of significant structural changes.

Key words: tin-titania binary oxides, template-assisted hydrothermal synthesis, methanol decomposition.

INTRODUCTION

In last decades, hydrogen was considered most effective fuel, but the problem with its safety storage and transport is still a matter of challenge. One reliable solution is to apply various chemical compounds, which in case of need easily release hydrogen. Among them, methanol gains much interest because it possesses high H/C ratio, releases hydrogen at relatively low temperatures, and can be synthesised from valuable and renewable sources by well-developed technologies. An important step in the control of this catalytic process is to develop highly efficient catalysts with regulated properties. Titania has received much attention due to its superior optical, electrical, mechanical, and catalytic properties combined with non-toxicity and cost effectiveness [1]. Dopant introduction into titania lattice is well known procedure to improve its dispersion and redox and catalytic properties due to a specific interaction and/or synergism between components [2]. It has been shown that incorporation of Sn^{4+} ions into the titania lattice increases its dispersion, provides significant structural and texture changes [3−5], and improves the photocatalytic activity [6].

Much effort has been focused on the preparation of Sn-Ti metal oxides with porous structure, high specific surface area, and good crystallinity by various synthetic routes, such as sol-gel, solvothermal, direct oxidation, electrodeposition, chemical/physical vapour deposition, emulsion or hydrolysis precipitation, etc. [7−10]. Among these procedures, the hydrothermal technique is considered suitable to prepare mesoporous mixed oxide materials of high surface area and pore volume [11]. However, to our knowledge no data on the preparation of binary titania-tin oxide materials by template-assisted hydrothermal technique have been reported. The aim of the present investigation was to prepare a series of titania-tin oxide materials of different Ti/Sn ratio. The effect of phase composition on their textural, structural, and redox properties was studied using a complex of various physicochemical techniques, such as nitrogen physicsorption, XRD, Raman, UV–Vis, FTIR, and TPR. The potential of application of these materials as catalysts was tested in methanol decomposition to syngas.

EXPERIMENTAL

Materials

TiO_2 and SnO_2 materials were synthesised by template-assisted technique using hexadecyl-N,N,N-trimethyl ammonium bromide (CTAB) as a template, hydrothermal treatment at 373 K, and calcination at 773 K [12]. The same synthesis was applied to prepare bi-component metal oxides. The samples were denoted as xTiySn, where x/y is the metal mol ratio, which was 2:8, 5:5, or 8:2.

Methods of characterisation

Specific surface area (A_{BET}) and total pore volume (V_{tot}) were measured by nitrogen adsorption-desorption isotherms at 77 K on a Beckman

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Coulter SA 3100 apparatus. Powder X-ray diffraction patterns were collected by a Bruker D8 Advance diffractometer with CuKα radiation and LynxEye detector; the average crystallite size was evaluated according to Scherrer equation. FTIR spectra (KBr pellets) were recorded on a Bruker Vector 22 FTIR spectrometer at a resolution of 1–2 cm^{-1} by accumulating 64–128 scans. Raman spectra were acquired by a DXR Raman microscope using a 780-nm laser. UV–Vis spectra were recorded on a Jasco V-650 UV–Vis spectrophotometer equipped with a diffuse reflectance accessory. Temperature-programmed reduction and thermogravimetric (TPR-TG) analysis was performed in a Setaram TG92 instrument in a flow of 50 vol.% H$_2$ in Ar (100 cm^3 min^{-1}) at a heating rate of 5 K.min^{-1}.

Catalytic tests

Methanol decomposition was carried out in a fixed-bed reactor at atmospheric pressure. The catalyst (0.055 mg) of 0.2–0.8-mm particle size was diluted with a three-fold higher amount (by volume) of glass spheres. Each catalyst was tested under conditions of a temperature-programmed regime within the range of 350–770 K at a heating rate of 1 K.min^{-1}. During the experiments, the reactant (methanol) as well as all carbon-containing products (CO, CO$_2$, methane, methyl formate, and dimethyl ether) were in the gaseous phase. Their amounts were determined by on-line GC analyses on a HP apparatus equipped with flame ionisation and thermal conductivity detectors, and a 30-m PLOT Q column using an absolute calibration method and a carbon-based material balance.

RESULTS AND DISCUSSION

To gain information about textural characteristics of the studied materials, nitrogen physisorption measurements were conducted (Fig. 1a, Table 1). The isotherms were characterised as type IV according to IUPAC classification, which is typical of mesoporous materials, with a hysteresis loop attributed to cage-like mesopores. All the materials were characterised by high specific surface area and total pore volume (Table 1). The binary materials demonstrated higher specific surface area in comparison with the individual metal oxides, which was the highest for 5Sn5Ti. Besides, formation of smaller and uniform mesopores was observed with the binary oxides. There was no simple relation between texture parameters (Table 1) and sample composition, which could be evidence for absence of mechanical mixture of the separate oxides. XRD patterns of TiO$_2$–SnO$_2$ mixed oxides are presented in Fig. 1b and data on phase composition, unit cell parameters, and average crystallite size are listed in Table 1.
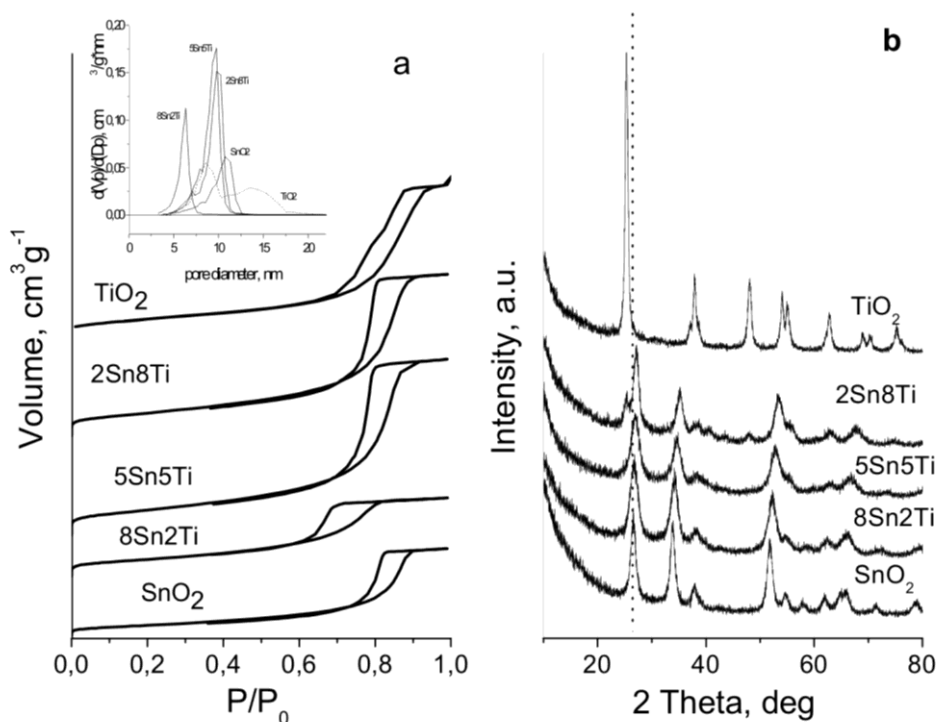

Fig. 1. Nitrogen physisorption isotherms (a) and pore size distribution (a, insert) and XRD patterns (b) for all Ti-Sn oxides.

For pure titania, only reflections of anatase (2θ = 25.6º, 38.3º, 47.8º, and 62.5º) were detected (pdf 01086-1157) [13]. The diffraction pattern of unmixed tin dioxide showed reflections at 2θ = 27.2° and 34.4° referred to SnO$_2$ with cassiterite tetragonal structure (ICDD card No. 41-1445) of space group P42/mnm. Weak reflections of anatase were still detected in the pattern of 8Ti2Sn, but well-defined reflections of cassiterite were also observed.

On further increase of tin content (5Ti-5Sn and 2Ti-8Sn samples) only reflections of well crystallised cassiterite were registered. These reflections were slightly shifted to higher Bragg angles indicating a decrease in cassiterite unit cell parameters.

Taking into account that Ti^{4+} and Sn^{4+} ion radii are 0.74 and 0.84 Å, respectively, the latter observation could be assigned to incorporation of the smaller Ti^{4+} ions into SnO$_2$ lattice [3]. A slight increase in anatase unit cell parameters was also detected with 2Sn8Ti (Table 1) probably due to incorporation of Sn^{4+} ions [3, 4]. XRD reflections of all the binary materials are broader as compared to the pure tin dioxide and titania, which is evidence for higher dispersion of the former (Table 1).

To obtain further information about the oxidation state of the various metal oxide species, UV-Vis, FTIR, and Raman spectroscopy measurements were also made (Fig. 2).

Table 1. Nitrogen physisorption and XRD data on Ti-Sn oxides of different composition.

Sample	A_{BET}, * m^2g^{-1}	V_{tot}, ** cm^3g^{-1}	Space group	Unit cell	Particle size, nm	SA***
TiO$_2$	85	0.29	anatase, I41/amd	3.7862(4) 9.493(1)	17	0.46
2Sn8Ti	98	0.30	cassiterite, P42/mnm	4.670(4) 3.059(2)	7	0.28
			anatase, I41/amd	3.803(3) 9.528(8)	10	
5Sn5Ti	107	0.32	cassiterite, P42/mnm	4.664(2) 3.096(2)	5	0.05
8Sn2Ti	72	0.14	cassiterite, P42/mnm	4.707(2) 3.154(1)	6	0.18
SnO$_2$	43	0.16	cassiterite, P42/mnm	4.738(1) 3.186(1)	9	0.21

*A_{BET} -specific surface area (BET method), **V_{tot}- total pore volume, ***SA - specific catalytic activity calculated per unit surface area at T = 700 K
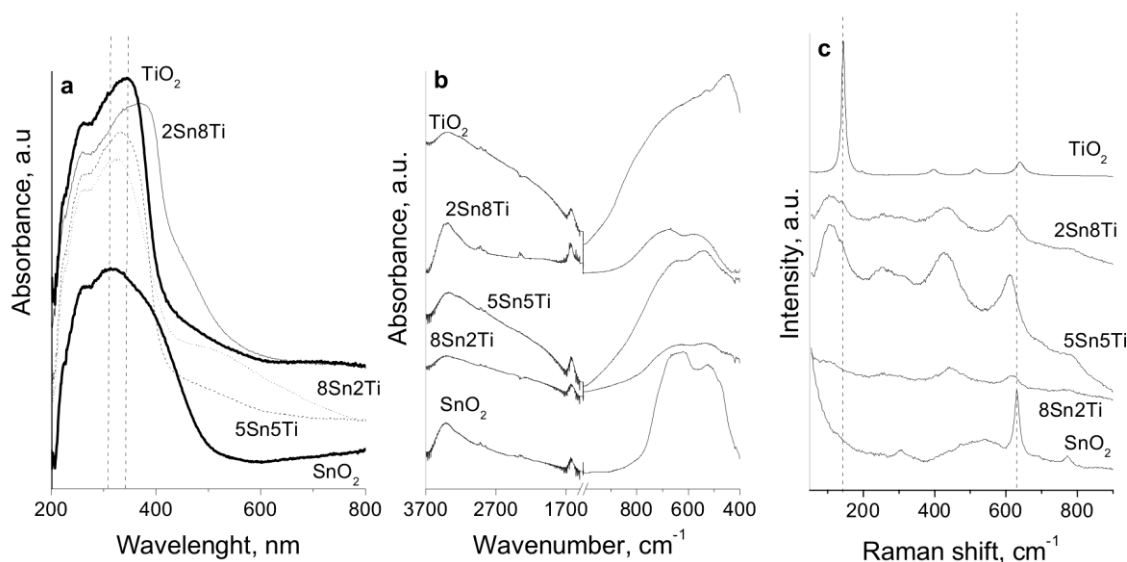

Fig. 2. UV-vis spectra (a), FTIR spectra (3700–1500 cm^{-1} and 1000–400 cm^{-1}) (b), and Raman spectra of the Ti-Sn oxides (c).

A strong absorption feature at 350 nm in the UV-Vis spectrum (Fig. 2a) of titania sample is due to d-d electronic transition between Ti^{4+} ions and O$_2$-

ligands in anatase [15]. The UV–Vis spectrum of pure tin dioxide represents an absorption in the 200–350-nm range, which is characteristic of a valence-

conduction interband transition. Increased absorption could be ascribed to the presence of defects in the SnO$_2$ lattice [16]. A maximum at about 230 nm could be due to surface Sn^{4+} species [15 and refs therein]. A well-defined red shift of the absorption edges was observed for all binary materials, which indicates changes in the environment and/or of the oxidation state of the tin ions.

FTIR spectra of TiO$_2$–SnO$_2$ materials are shown in Fig. 2b. The IR bands at about 460, 620 cm^{-1} and the shoulder at 910 cm^{-1} are close to reported reference vibration modes of Ti–O in anatase phase TiO$_2$ lattice [17]. Changes in the shape and intensity of the shoulder at 910 cm^{-1} in the IR spectra of the bi-component materials reveal interaction between tin dioxide and titania phases, which is in good agreement with XRD and nitrogen physisorption data. In consistence with the UV-Vis data (Fig.2a), the broad band in the 400–680 cm^{-1} region could be ascribed to superposition of vibration stretching modes of bridged Sn−O−Sn, Ti−O−Ti, and Ti−O−Sn bonding [17]. Broad bands centred at about 3400 and 1600 cm^{-1}, which are generally assigned to stretching and bending vibrations of physically adsorbed water and hydroxyl groups, respectively, were registered as well [18,19].

To get more information on the interaction between the metal oxide nanoparticles, Raman spectra were also recorded (Fig. 2c). The spectrum of titania sample (Fig. 2c) displays the main peaks at 149, 198, 398, 515, and 644 cm^{-1} that are typical of anatase TiO$_2$ structure [20]. The spectrum of tin dioxide consists of an intense band at 630 cm^{-1} and a weak band at 774 cm^{-1}, which could be assigned to [21] A1g and B2g modes of symmetric and asymmetric stretching vibrations of Sn−O bonds, respectively [22, 23].

A slight shift and broadening of the main Raman-active modes combined with a decreased intensity were observed with the bi-component materials (Fig. 2c), which could be assigned to partial incorporation of titanium ions into the SnO$_2$ lattice. The latter resulted in significant changes in dispersion and structure [21−23].

Fig. 3 shows data on TPR analyses. Reduction of tin dioxide sample was initiated above 440 K. A further temperature increase up to 773 K caused a weight loss associated with about 100% (или: with almost complete) reduction of Sn^{4+} to Sn^0 (Fig. 3a).

The TPR-DTG effect on the bi-component samples was smaller in comparison with unmixed tin dioxide and shifted to higher temperature. In accordance with the UV–Vis data, this could be assigned to the formation of hardly reducible Ti-O-Sn species. 5Sn5Ti manifested the lowest reducibility. Note that this material exhibited the highest dispersion and specific surface area (Table 1). In this way, the equimolar Ti/Sn ratio in the binary materials facilitated the formation of homogeneous mixed oxide phase.

Temperature dependencies of methanol conversion and the selectivity to CO for the titania and tin oxide materials are presented in Fig. 4a, b.
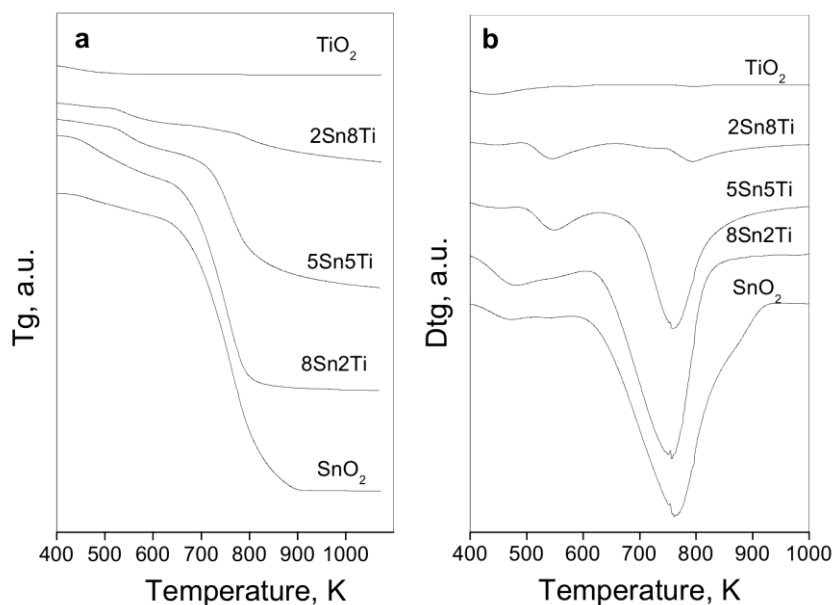

Fig. 3. TPR-TG (a) and TPR-DTG (b) profiles of the Ti-Sn mixed oxides.
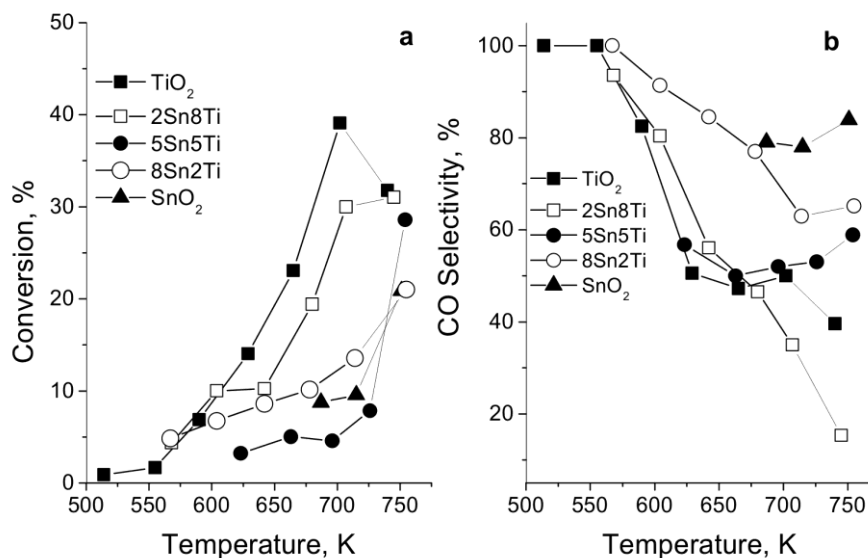
Fig. 4. Methanol conversion vs temperature (a) and selectivity to CO (b) for the Sn-Ti oxides.

Except for CO, which is directly associated with hydrogen production from methanol, CO_2, CH_4, and dimethyl ether (DME) were registered as by-products. All samples exhibited catalytic activity above 550 K. It was the highest for pure titania and strongly decreased upon SnO_2 addition. No simple relation between catalytic activity and samples composition was observed. Moreover, the sample having the highest dispersion and specific surface area (5Sn5Ti) demonstrated the lowest catalytic activity. Specific catalytic activity per unit surface area (SA) was calculated to disregard the impact of sample texture parameters on the catalytic properties (Table 1). Again, the highest value was found for titania, whereas 5Sn5Ti demonstrated an extremely low value. At the same time, significant differences in products distribution were observed. The main by-product on titania was DME (about 40%), which could be assigned to high Lewis acidic functionality [25]. The highest CO selectivity (85%) was detected for pure tin dioxide. All binary materials showed a relatively high selectivity to CO_2 (up to 10%) and methane (25−47%) formation. These results clearly demonstrate changes of the catalytic sites in the binary materials. In view of the XRD, TPR, UV-Vis, and Raman and FTIR spectral data, formation of shared Sn−O−Ti active sites can be proposed. Obviously, this formation is associated with sample composition, being to a higher extent for the sample with Ti/Sn equimolar ratio.

CONCLUSIONS

High surface area mesoporous SnO_2-TiO_2 binary materials can be successfully synthesized using template assisted hydrothermal technique. It was found that the binary oxide materials exhibit higher dispersion and specific surface area, but lower specific catalytic activity and selectivity in methanol decomposition to CO as compared to the individual metal oxides. This could be assigned to the formation of shared Sn−O−Ti structures, the process being directed by the Ti/Sn ratio.

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НАНОСТРУКТУРИРАНИ МЕЗОПОРЕСТИ Ti$_x$Sn$_{1-x}$O$_4$ СМЕСЕНИ ОКСИДИ КАТО КАТАЛИЗАТОРИ ЗА РАЗПАДАНЕ НА МЕТАНОЛ: ЕФЕКТ НА СЪОТНОШЕНИЕТО Ti/Sn

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(Резюме)

Целта на настоящето изследване е да се изясни влиянието на Ti / Sn съотношението на смесени Ti$_x$Sn$_{1-x}$O$_4$ оксиди върху техните структурни, редукционни и каталитични свойства. Мезопорести смесени оксиди с различно съотношение Ti/Sn са синтезирани чрез хидротермална техника в присъствие на органичен темплейт. Получените материали са характеризирани с комплекс от физикохимични техники, като асорбция на азот, рентгенофазов анализ, Раманова, УВ-видима и ИЧ спектроскопия и ТПР с водород. Като каталитична тест-реакция е използвана реакция на разпадане на метанол до синтез газ. Каталитичната активност на бинарните материали зависи по сложен начин от техния фазов състав. Той е подобрен благодарение на увеличаването на специфичната повърхност и обема на порите, но силно потиснат поради значителните структурни промени.