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## STRUCTURE AND PROPERTIES OF WO<sub>3</sub>-ZrO<sub>2</sub> GEL COMPOSITES AS POTENTIAL CATALYSTS FOR HYDROCARBONS ISOMERIZATION PROCESS

### STRUKTURA I WŁAŚCIWOŚCI KOMPOZYTÓW ŻELOWYCH WO<sub>3</sub>-ZrO<sub>2</sub> JAKO POTENCJALNYCH KATALIZATORÓW W PROCESIE IZOMERYZACJI WĘGLOWODORÓW

Tungsten oxide dispersed on zirconia in WO<sub>3</sub>-ZrO<sub>2</sub> system found application as strong acidic catalyst in hydrocarbons isomerization process.

Specific method for synthesis of gel metal oxide composites based on Complex Sol-Gel Process (CSGP) were elaborated in Institute of Nuclear Chemistry and Technology, Warsaw. Structural investigations of WO<sub>3</sub>-ZrO<sub>2</sub> gel composites thermally treated at 500°C, 650°C and 800°C using X-ray diffraction (XRD) and scanning electron microscopic (SEM) methods were carried out. The gel composites annealed at 500°C appears as amorphous material, in the composites thermally treated at 650°C beginning of crystalline forms are observed. The gel composites annealed at 800°C are polycrystalline.

Both oxides exist as separate crystalline phases, ZrO<sub>2</sub> in the high symmetry forms: cubic and tetragonal, WO<sub>3</sub> in the monoclinic form.

*Keywords:* WO<sub>3</sub>-ZrO<sub>2</sub> gel composites, structure investigations, hydrocarbons isomerisation process, XRD, thermal analysis, SEM

Tlenek wolframu dyspergowany w tlenku cyrkonu znalazł zastosowanie jako silnie kwaśny katalizator w procesie izomeryzacji węglowodorów. Zaproponowano specyficzną metodę syntezy kompozytów żelowych tlenków metali bazującą na opracowanym w Instytucie Chemii i Techniki Jądrowej w Warszawie Kompleksowym Procesie Zol-Żel. Badania strukturalne kompozytów żelowych WO<sub>3</sub>-ZrO<sub>2</sub> poddanych termicznej obróbce w temperaturach 500°C, 650°C, 800°C. prowadzono stosując metody dyfrakcji promieniowania rentgenowskiego (XRD) oraz skaningowej mikroskopii elektronowej (SEM). Żele wygrzewane w temperaturze 500°C okazały się materiałem amorficznym, w kompozytach wygrzewanych w temperaturze 650°C zaobserwowano pojawienie się form krystalicznych. Natomiast żele wygrzewane w temperaturze 800°C posiadały strukturę polikrystaliczną. Oba tlenki występują jako oddzielne fazy krystaliczne, ZrO<sub>2</sub> w postaci faz regularnej i tetragonalnej oraz WO<sub>3</sub> w postaci fazy jednoskośnej.

### 1. Introduction

The tungsten oxide-zirconium oxide composites have been recognized as catalysts with strong acid properties [1] and they have found applications as catalysts in the process of isomerization of parafines. The advantage of these compounds with comparison to previously used sulfates is that they do not lose dopant during heat treatment and deactivation extent. is smaller in this case.

In accessible scientific literature the authors stress that strong acid properties is connected with the formation of WO<sub>3</sub> micro-areas. This hypothesis has been confirmed by several experimental observations: such as the increase in activity with the percentage contents of

tungsten, the need of compounds heating to the temperature where sintering begins to become evident, as well as observation in the Raman spectrum the lines corresponding to the clusters of WO<sub>3</sub>. D.G.Barton et al. [2] reported that, in the tungsten oxide –zirconium oxide composite the isolated atoms of tungsten are in slightly deformed octahedral positions and that is no tetrahedral tungsten in this case J.M Parera et al. [3] present catalysts based on tungsten oxide on zirconia support which are prepared starting from solution of ammonium metatungstate at pH = 6 or more. Tungsten, in the form of single layer on support, exists in tetrahedral positions but sometimes appears in octahedral positions which become dominant when amount of tungsten deposited increases. Sohn and

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J. Park [4] prepared  $\text{WO}_3\text{-ZrO}_2$  catalysts containing only 5% of tungsten with a Raman line at  $935\text{cm}^{-1}$  attributed to positions of tetrahedral types. However this line disappears and was replaced by other which is attributed to the octahedral tungsten with the tungsten content increasing up to 13%.

In the presented paper for preparation of  $\text{WO}_3\text{-ZrO}_2$  gel composites the Complex Sol-Gel Process elaborated in Institute of Nuclear Chemistry and Technology has been proposed [5,6]. Investigation of structure and properties of synthesized composites is the main purpose of presented work.

## 2. Experimental procedure

### 2.1. Chemicals for synthesis of gel metal-oxide composites

The following reagents have been used for synthesis of gel composites:

Ammonium tungsten oxide pentahydrate 99.999% obtained from Alfa Aesar,

Zirconyl nitrate hydrate 99.99% obtained from Sigma-Aldrich,

Ascorbic acid, pharmaceutical grade from Teakea Europe GmbH, Hamburg,

TEOS-Tetraethylosilane >98% p.a from Fluka.

### 2.2. Synthesis

The synthesis of zirconium-tungstate  $\text{WO}_3\text{-ZrO}_2$  composites with different molar ratio of metal oxides 1:1, 1:2 and 3:2 were prepared by CSGP method [5]. The initial stage of the process is preparation of ammonium tungstate ascorbate sol next the separately prepared zirconyl, titanium sols are added gradually to the reaction mixture. When the gelation is over, the gel are thermally treated at temperature indicated by thermal analysis. Flow-chart of synthesis is presented in Fig. 1.

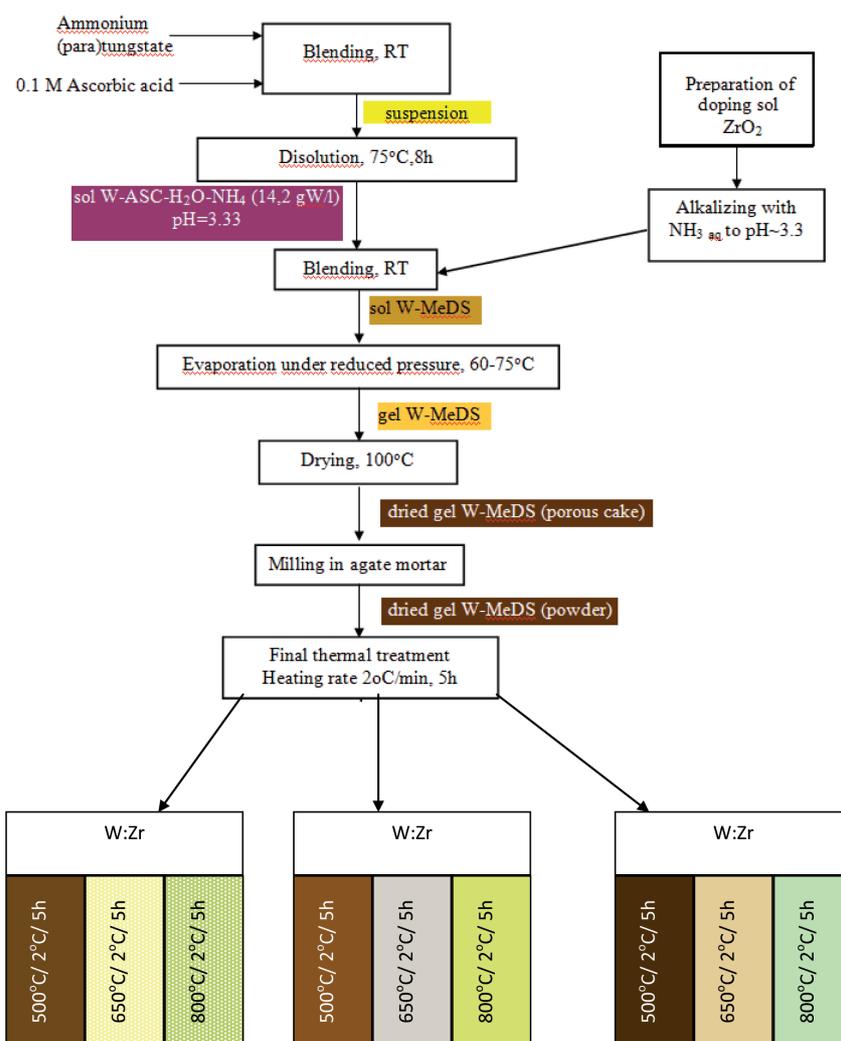


Fig. 1. Flow-chart of  $\text{WO}_3\text{-ZrO}_2$  composite synthesis

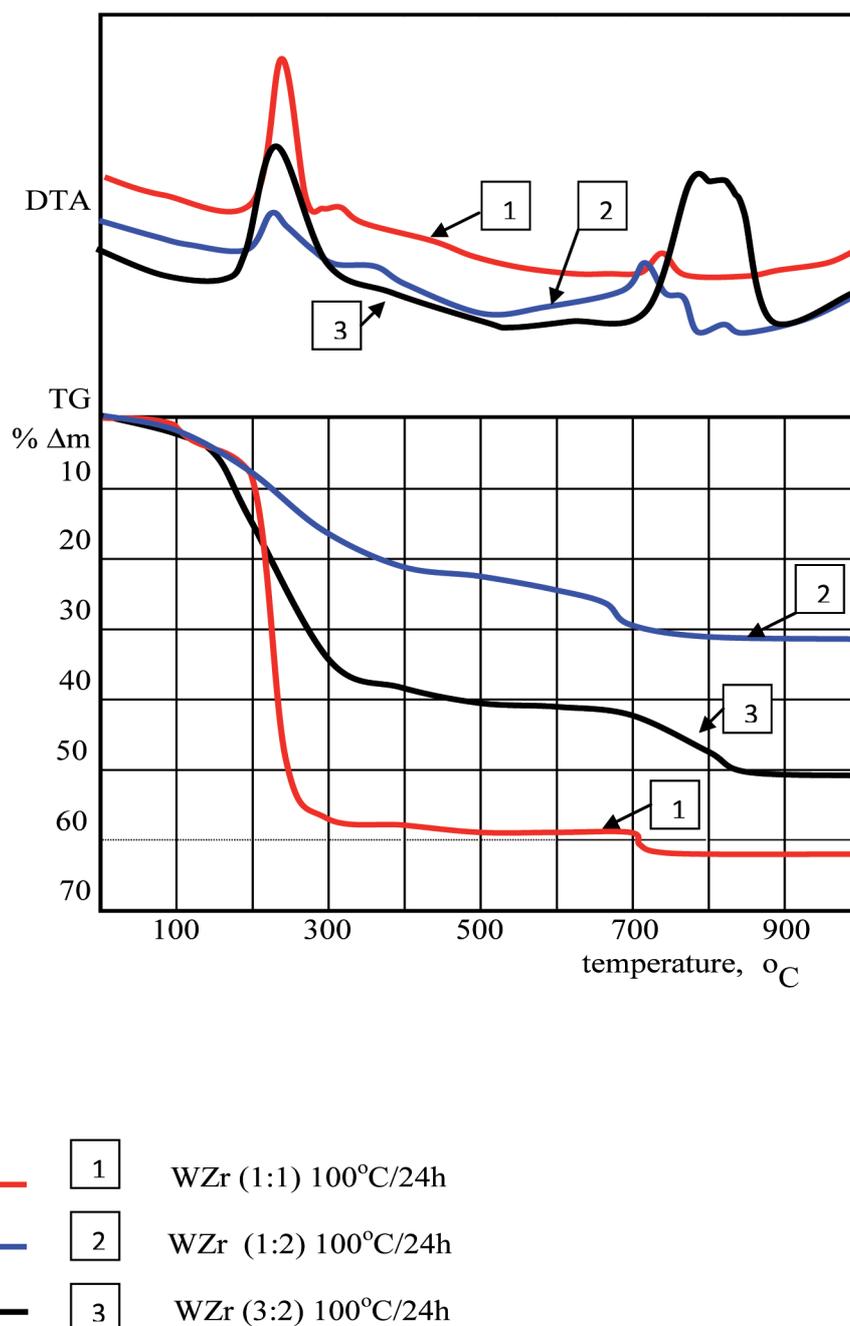


Fig. 2. Thermal analysis of  $\text{WO}_3\text{-ZrO}_2$  composites, TG and DTA curves

The gels were annealed accordingly to the temperatures indicated by thermal analysis; 500°C, 650°C, 800°C. Weight loss curves (TG) were determined by thermogravimetry using Paulik-Paulik Erdey system with MOM Derivatograph. The composites samples of 100 mg weight are heated from room temperature up to 1000°C with the rate 10°C/min in flowing air. The TG and DTA curves for investigated samples have been shown in Fig. 2.

The TG and DTA curves of  $\text{WO}_3\text{-ZrO}_2$  samples indicates for few stages of weight loss. First correspond to desorption of the water molecules adsorbed on particles

surface, removal of nitrates, ammonium, and methyl groups as well as creation of W-O bonds. The peaks in temperature range 240-280°C indicates on running of exothermic reactions, with taking part of above mentioned reagents. Next exothermic reactions we can observe in temperature range 700-780°C, connected with transition gel composites from amorphous form to crystalline phase. It is worthwhile to remark the slight displacement of these last peaks in DTA curve in the dependence on the molar ratio  $\text{WO}_3$  to  $\text{ZrO}_2$  in investigated samples.

### 2.3. X-ray diffraction study

The samples of composites were analyzed by X-ray diffraction technique using a Rigaku Miniflex diffractometer with Cu-K $\alpha$  radiation (tube output voltage 30kV, current 15mA) and scanning range from  $2\theta = 3^\circ$  to  $2\theta = 90^\circ$  (step 0.02 and rate  $2^\circ/\text{min}$ ). In the diffraction patterns of composites annealed at  $500^\circ\text{C}$  there is rather no peaks, whereas in the X-ray diffraction patterns  $\text{WO}_3\text{-ZrO}_2$  (1:1, 1:2, 3:2) composites annealed at  $650^\circ\text{C}$ , the some group of peaks occurring above background level are observed. The gels annealed at  $800^\circ\text{C}$  are fully polycrystalline.

Both oxides exist as separate crystalline phase:  $\text{ZrO}_2$  in a high symmetry forms cubic and tetragonal,  $\text{WO}_3$  in monoclinic form [6]. The X-ray diffraction patterns of  $\text{WO}_3\text{-ZrO}_2$  (1:2) composite annealed at the above temperatures have been shown in Fig. 3.

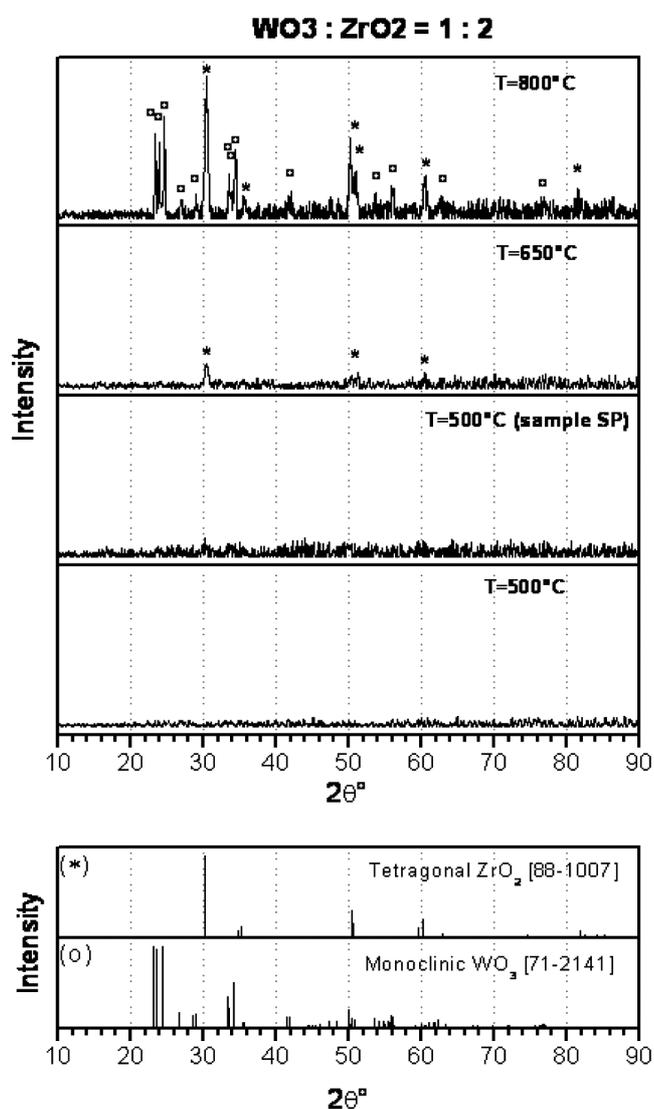


Fig. 3. X-ray diffraction patterns of  $\text{WO}_3\text{-ZrO}_2$  gels annealed at  $500^\circ\text{C}$ ,  $650^\circ\text{C}$ ,  $800^\circ\text{C}$

Due to X-ray scattering dependence on atomic number of studied elements  $\text{WO}_3$  peaks are generally stronger than that of  $\text{ZrO}_2$ . Therefore composite with proportion  $\text{WO}_3 - \text{ZrO}_2$  (1:2) is specially chosen in order to obtain similar strongest peaks intensities for both oxides which may be illustrated in Fig. 3 for sample annealed at  $800^\circ\text{C}$ . Particular peaks may be identified with attached JCPDS standards.

For estimation of crystallite dimensions in particular crystalline phases forming above composites the Scherrer equation was applied

$$D_{hkl} = k\lambda 360 / (\beta \cos\theta 2\pi)$$

where

$D_{hkl}$  – average crystallite dimensions perpendicular to the reflecting plane,

$\lambda$  – wave length,

$k$  – Scherrer constant,

$\theta$  – diffraction angle,

$\beta$  – diffraction peak half-width

Calculations were done for  $\lambda = 1.542\text{\AA}$  (Cu anode) and  $k=0.89$ . The obtained data has been presented in Table 1.

TABLE 1

Dimensions of crystallites in  $\text{WO}_3\text{-ZrO}_2$  gel composites annealed at  $800^\circ\text{C}$

		$2\theta$	$\theta$	$\cos\theta$	$\beta$	$D_{hkl}$
$\text{WO}_3\text{-ZrO}_2$	3:2	$\text{WO}_3$	$23,36^\circ$	$11,68^\circ$	0,9793	$0,20^\circ$ $D_{002} = 401\text{\AA}$
		$\text{ZrO}_2$	$30,44^\circ$	$15,22^\circ$	0,9649	$0,55^\circ$ $D_{101} = 148\text{\AA}$
	1:1	$\text{WO}_3$	$23,34^\circ$	$11,87^\circ$	0,9786	$0,28^\circ$ $D_{002} = 287\text{\AA}$
		$\text{ZrO}_2$	$30,46^\circ$	$15,23^\circ$	0,9649	$0,58^\circ$ $D_{101} = 140\text{\AA}$
	1:2	$\text{WO}_3$	$23,38^\circ$	$11,69^\circ$	0,9793	$0,20^\circ$ $D_{002} = 401\text{\AA}$
		$\text{ZrO}_2$	$30,42^\circ$	$15,21^\circ$	0,9650	$0,50^\circ$ $D_{101} = 163\text{\AA}$

As can be seen the crystallite sizes of both phases differ each other.  $\text{ZrO}_2$  crystallite sizes are considerably smaller than that of  $\text{WO}_3$ . Between  $\text{ZrO}_2$  polymorphic forms tetragonal form shows smallest crystallite sizes. But values obtained for  $\text{WO}_3$  may be connected with agglomeration of some nanocrystals.

Important parameter of catalytic materials characterization, which will be used as a powder is specific surface. In the Table 2 the change of  $\text{WO}_3\text{-ZrO}_2$  specific surface data with increasing temperature of thermal treatment have been presented.

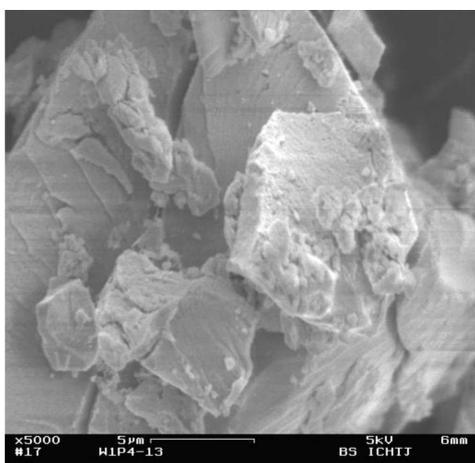
We can observe the increasing of specific surface values of  $\text{WO}_3\text{-ZrO}_2$  (1:2) composite with annealed temperature. The samples of thermal treatment at  $800^\circ\text{C}$  achieved the value of specific surface near to  $28\text{ m}^2/\text{g}$ .

TABLE 2  
 Specific surface data of WO<sub>3</sub>-ZrO<sub>2</sub> (1:2) composite

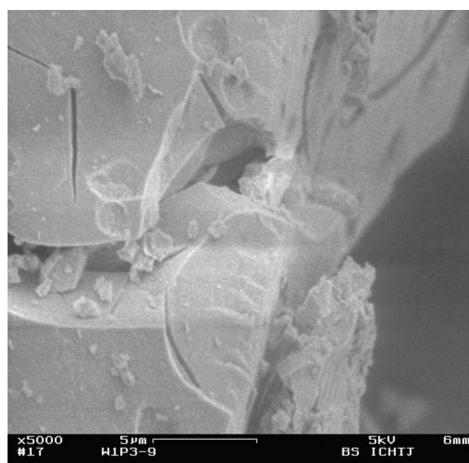
Number of sample	Parameters of synthesis	Specific surface [m <sup>2</sup> /g]
1	110°C / 24 h	0,93
2	200°C / 2 h	11,9
3	350°C / 5 h	8,3
4	350°C / 5 h + 500°C / 5 h	8,4
5	500°C / 5 h	13,2
6	650°C / 5 h	15,7
7	800°C / 5 h	27,7

Increase of specific surface values of WO<sub>3</sub>-ZrO<sub>2</sub> composites with growth of temperature of their thermal treatment can be also documented by means of SEM micrographs (Fig. 4). Surface changes directed to small crystallites forming of precise sizes may be observed especially for samples annealed at 800°C. Some agglomerates are still remaining.

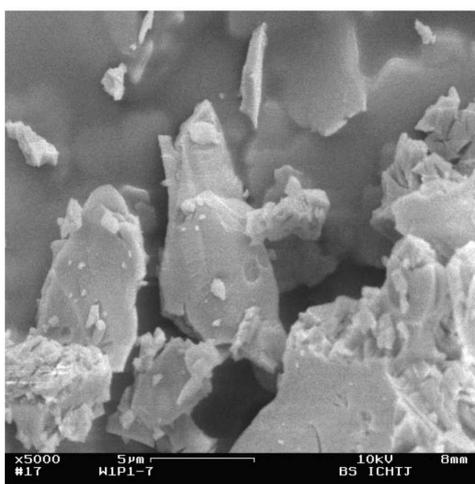
The adhesion degree of catalytic materials to different surfaces and porosity degree obtained layers allows us to determination of active surface of catalyst. The several trials of adhesive spread of WO<sub>3</sub>-ZrO<sub>2</sub> gels on nickel, titanium and glass plates were performed. The results of experiments for Ni substrate are shown on SEM micrographs (Fig. 5). The central part of image from Fig. 5a is visible at higher magnification in Fig. 5b.



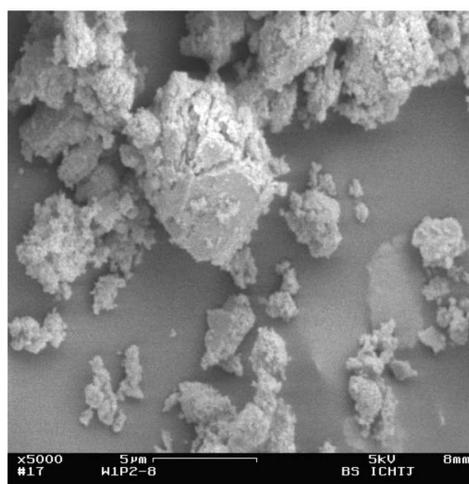
(a)



(b)



(c)



(d)

 Fig. 4. SEM images of WO<sub>3</sub>- ZrO<sub>2</sub> (1:2) gels, (a) 110°C, (b) 200°C, (c)500°C, (d) 800°C

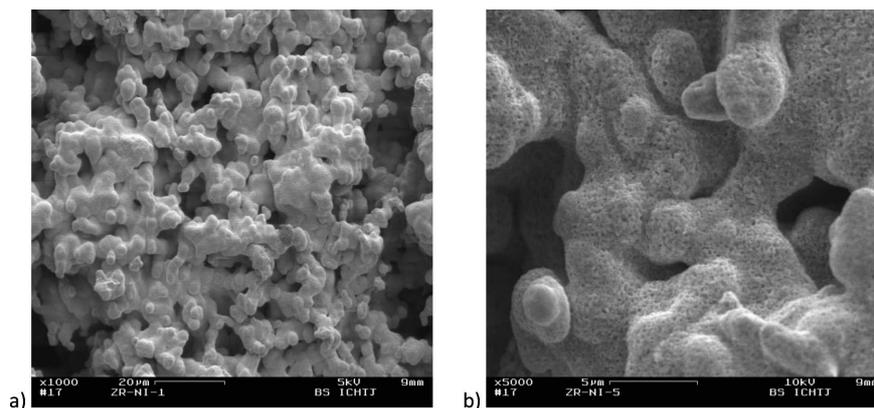


Fig. 5. The surface layer of  $\text{WO}_3\text{-ZrO}_2$  gel composites on nickel: a)  $\times 1\,000$ , b)  $\times 5\,000$

### 3. Discussion of results

Composites obtained by the CSGP method appear as amorphous or polycrystalline in the dependence on annealing temperature. Chemical reactions during gel-sol process are finished after gel annealing with crystalline phases forming. The results of XRD studies show that low temperature annealing gives amorphous phases with only short range order. The beginning of crystalline phase forming is observed in composites annealed at  $650^\circ\text{C}$ . Composites annealed at  $800^\circ\text{C}$  are polycrystalline. These X-ray results are confirmed by TG and DTA curves.

Both oxides exist as separate crystalline phases. However  $\text{WO}_3$  shows stabilising effect to higher symmetry  $\text{ZrO}_2$  forms which normally not exist at ambient temperature. This situation is similar to that encountered in  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  composites [7]. Common phase of tungstate type reported by Lambrecht et al. form in other conditions [8]. Planned experiments with long time gels annealing may explain whether such phases may appear in our materials.

Crystallites dimensions counted by Scherrer formula show the sizes difference in both oxides. Tetragonal  $\text{ZrO}_2$  has smaller crystallite sizes than other crystal forms of this compound. One can suppose that  $\text{WO}_3$  crystallites are agglomerates of smaller nano crystallites which may be the cause of above mentioned catalytic effects.

Forming of crystalline phases is accompanied by microstructure changes observed by SEM method. The specific surface values are higher for crystalline phases. Scanning transmission electron microscopy methods (STEM) with higher resolving power would be useful to detect morphological changes in nano scale connected with catalytic effects.

On the basis of obtained results the following conclusions may be written

1. The degree of crystallinity for studied composite depends on annealing temperature. Polycrystalline

structure is observed after annealing at  $800^\circ\text{C}$ .  $\text{WO}_3$  exists in monoclinic form,  $\text{ZrO}_2$  is mainly tetragonal with some amount of cubic phase.

2. Crystallite  $\text{ZrO}_2$  sizes are smaller than that of  $\text{WO}_3$ .
3. The appearance of crystalline phases is accompanied by microstructure changes.
4. The carried out investigations proved, that tested selective properties of  $\text{WO}_3\text{-ZrO}_2$  gel composites, synthesized by means of CSGP, indicate proper features as potential catalysts for hydrocarbons isomerization process. The described method of  $\text{WO}_3\text{-ZrO}_2$  composites synthesis can be used for preparation of these potential catalysts.

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