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STRUCTURE AND PROPERTIES OF WO_3-ZrO_2 GEL COMPOSITES AS POTENTIAL CATALYSTS FOR HYDROCARBONS ISOMERIZATION PROCESS

STRUKTURA I WŁAŚCIWOŚCI KOMPOZYTÓW ŻELOWYCH WO_3-ZrO_2 JAKO POTENCJALNYCH KATALIZATORÓW W PROCESIE IZOMERYZACJI WĘGLOWODORÓW

Tungsten oxide dispersed on zirconia in WO_3-ZrO_2 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_3-ZrO_2 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_2 in the high symmetry forms: cubic and tetragonal, WO_3 in the monoclinic form.

Keywords: WO_3-ZrO_2 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_3-ZrO_2 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_2 w postaci faz regularnej i tetragonalnej oraz WO_3 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_3 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_3. 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 WO_3-ZrO_2 catalysts containing only 5% of tungsten with a Raman line at 935cm^{-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 WO_3-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, pharmaceutic grade from Teakea Europe GmbH, Hamburg,

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

2.2. Synthesis

The synthesis of zirconium-tungstate WO_3-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.

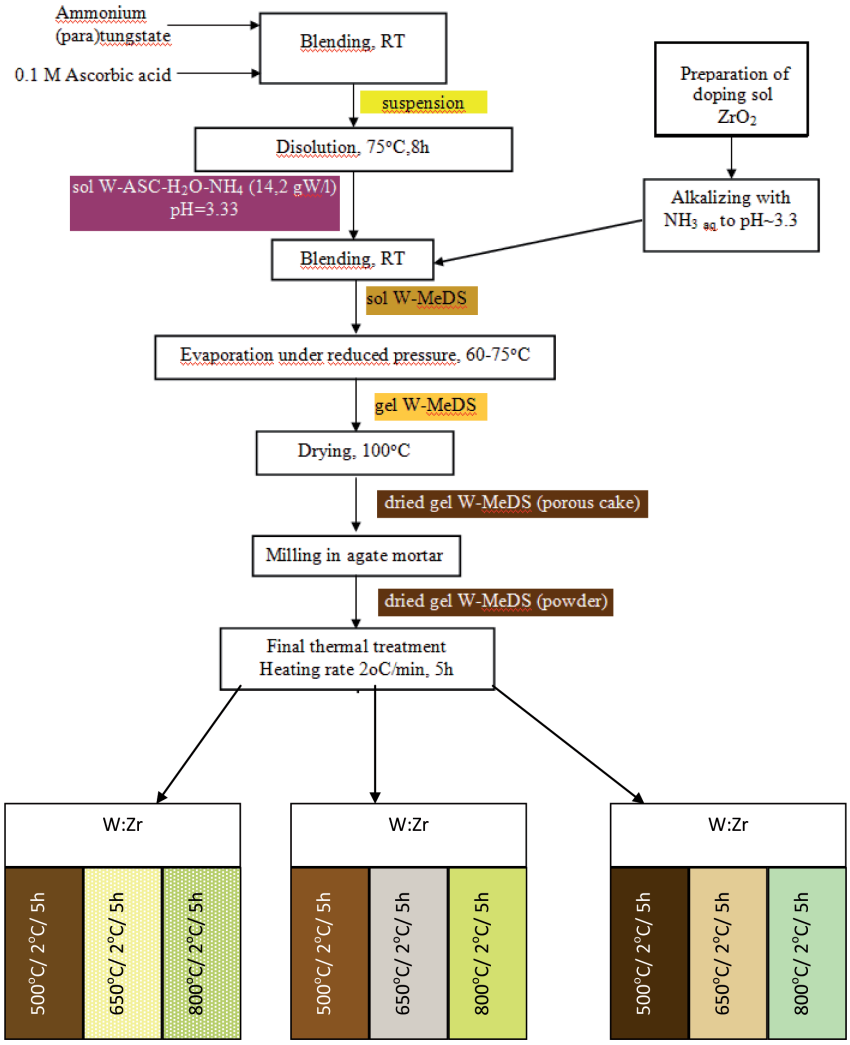

Fig. 1. Flow-chart of WO_3-ZrO_2 composite synthesis

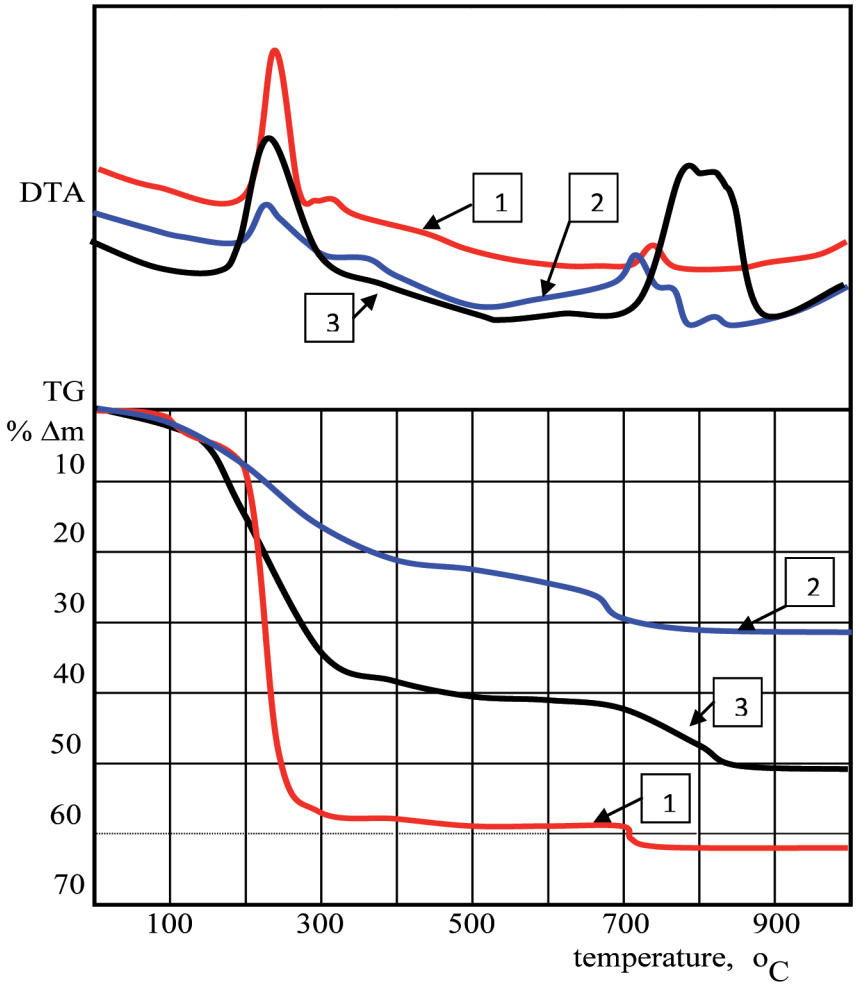

Fig. 2. Thermal analysis of WO_3-ZrO_2 composites, TG and DTA curves

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 WO_3-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 WO_3 to 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-Kα radiation (tube output voltage 30kV,current 15mA) and scanning range from 2Θ =3° to 2Θ =90° (step 0.02 and rate 2°/min). In the diffraction patterns of composites annealed at 500°C there is rather no peaks, whereas in the X-ray diffraction patterns WO_3-ZrO_2 (1:1,1:2, 3:2) composites annealed at 650°C, the some group of peaks occurring above background level are observed. The gels annealed at 800°C are fully polycrystalline.

Both oxides exist as separate crystalline phase:. ZrO_2 in a high symmetry forms cubic and tetragonal, WO_3 in monoclinic form [6]. The X-ray diffraction patterns of WO_3-ZrO_2 (1:2) composite annealed at the above temperatures have been shown in Fig. 3.

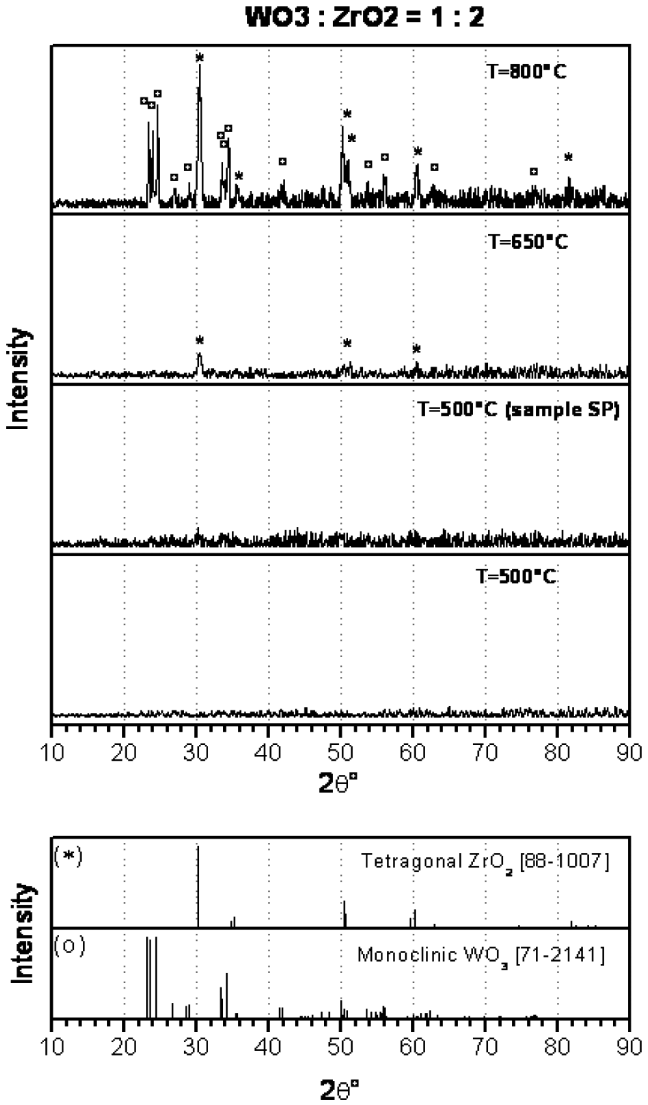

Fig. 3. X-ray diffraction patterns of WO_3-ZrO_2 gels annealed at 500°C, 650°C, 800°C

Due to X-ray scattering dependence on atomic number of studied elements WO_3 peaks are generally stronger than that of ZrO_2. Therefore composite with proportion WO_3 – 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°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,

λ– wave length,

k – Scherrer constant,

θ– diffraction angle,

β– diffraction peak half-width

Calculations were done for λ =1.542Ŕ (Cu anode) and k=0.89. The obtained data has been presented in Table 1.

TABLE 1
Dimensions of crystallites in WO_3-ZrO_2 gel composites annealed at 800°C

			2θ	θ	cosθ	β	D_{hkl}
WO_3-ZrO_2	3:2	WO_3	23,36°	11,68°	0,9793	0,20°	D_{002} =401Å
		ZrO_2	30,44°	15,22°	0,9649	0,55°	D_{101} =148Å
	1:1	WO_3	23,34°	11,87°	0,9786	0,28°	D_{002} =287Å
		ZrO_2	30,46°	15,23°	0,9649	0,58°	D_{101} =140Å
	1:2	WO_3	23,38°	11,69°	0,9793	0,20°	D_{002} =401Å
		ZrO_2	30,42°	15,21°	0,9650	0,50°	D_{101} =163Å

As can be seen the crystallite sizes of both phases differ each other. ZrO_2 crystallite sizes are considerably smaller than that of WO_3. Between ZrO_2 polymorphic forms tetragonal form shows smallest crystallite sizes. But values obtained for 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 WO_3-ZrO_2 specific surface data with increasing temperature of thermal treatment have been presented.

We can observe the increasing of specific surface values of WO_3-ZrO_2 (1:2) composite with annealed temperature. The samples of thermal treatment at 800°C achieved the value of specific surface near to 28 m^2/g.

TABLE 2
Specific surface data of WO3-ZrO2 (1:2) composite

Number of sample	Parameters of synthesis	Specific surface [m^2/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_3-ZrO_2 composites with growth of temperature of theirs 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_3-ZrO_2 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.

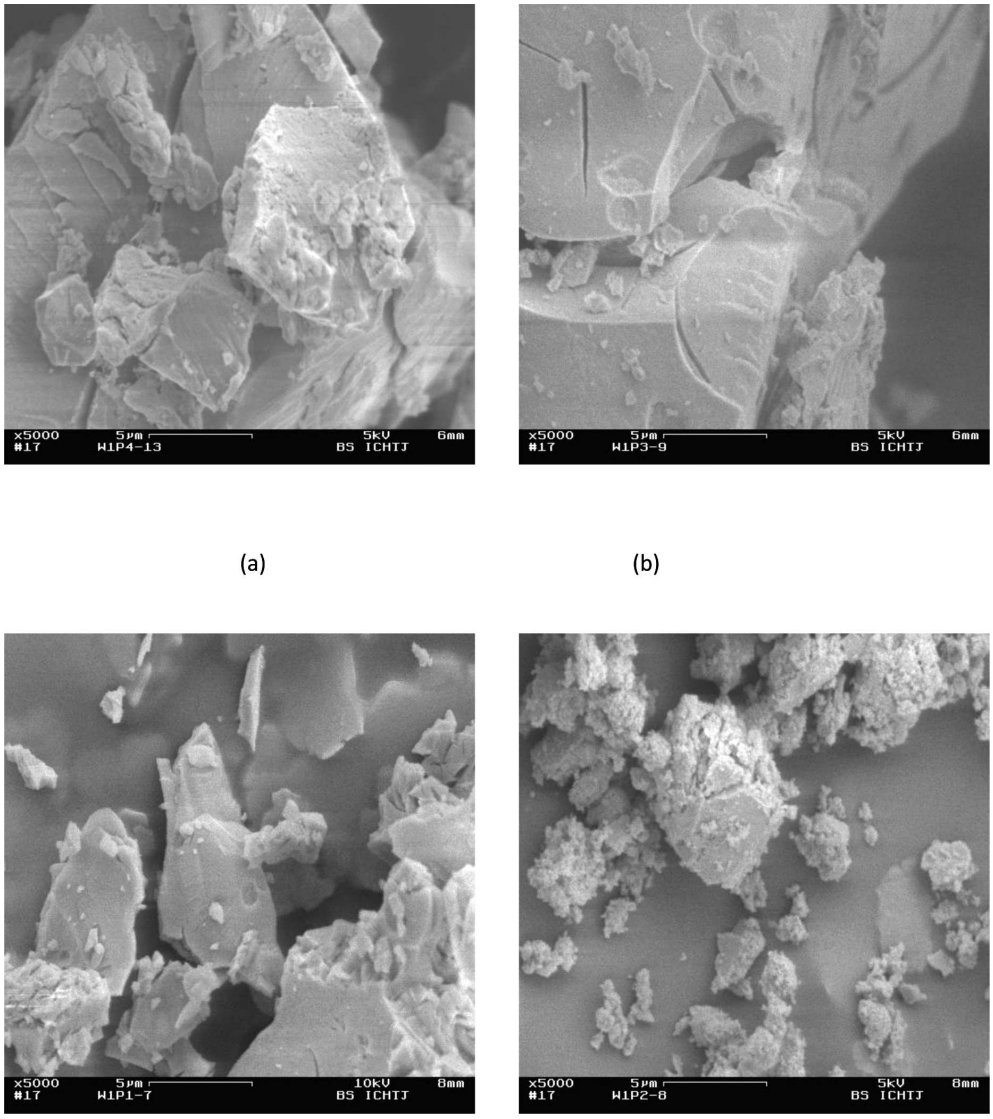

Fig. 4. SEM images of WO_3- ZrO_2 (1:2) gels, (a) 110°C, (b) 200°C, (c)500°C, (d) 800°C

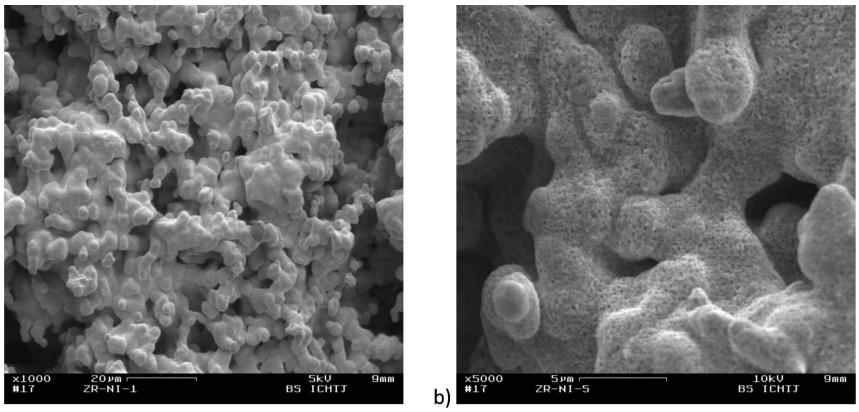

Fig. 5. The surface layer of WO_3-ZrO_2 gel composites on nickel: a) x 1 000, b) x 5 000

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°C. Composites annealed at 800°C are polycrystalline. These X-ray results are confirmed by TG and DTA curves.

Both oxides exist as separate crystalline phases. However WO_3 shows stabilising effect to higher symmetry ZrO_2 forms which normally not exist at ambient temperature. This situation is similar to that encountered in Al_2O_3–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 ZrO_2 has smaller crystallite sizes than other crystal forms of this compound. One can suppose that 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°C. WO_3 exists in monoclinic form, ZrO_2 is mainly tetragonal with some amount of cubic phase.
2. Crystallite ZrO_2 sizes are smaller than that of WO_3.
3. The appearance of crystalline phases is accompanied by microstructure changes.
4. The carried out investigations proved, that tested selective properties of WO_3-ZrO_2 gel composites, synthesized by means of CSGP, indicate proper features as potential catalysts for hydrocarbons isomerization process. The described method of WO_3-ZrO_2 composites synthesis can be used for preparation of these potential catalysts.

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