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Synthesis of vanadium-enriched oxide materials via modified sol-gel route with the use of waste solutions contaminated with vanadium ions

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Abstract: In this study, the synthesis of zirconia as well as zirconia enriched with vanadium by modified sol-gel method was presented. The modification of the method was based on the replacement of the traditional basic promoter of hydrolysis, which is ammonia, with sodium hydroxide solution. The most favorable conditions for the synthesis of zirconium with a new hydrolysis promoter were selected. A comparative analysis of ZrO₂ obtained using various hydrolysis promoters was performed. Both materials exhibited almost the same physicochemical properties, which proves that in this case the nature of the hydrolysis promoter used in sol-gel route does not significantly affect the properties of the ZrO₂. Then, synthesis of ZrO₂/V systems was carried out using model and real solutions containing vanadium ions as hydrolysis promoters. The solutions formed after vanadium catalyst leaching were used as real solutions. The effect of vanadium concentration and the presence of impurities on the final physicochemical properties of the obtained hybrid materials were investigated via scanning electron microscopy (SEM), dynamic light scattering (DLS), energy-dispersive X-ray microanalysis (EDS), Fourier transform infrared spectroscopy (FT-IR), low-temperature nitrogen sorption (BET), thermogravimetric analysis (TGA). The analysis of the obtained results allows to state that the developed technique for the synthesis of ZrO₂ and ZrO₂/V systems, using a modified sol-gel method, enabled the production of attractive materials.

Keywords: modified sol-gel method, zirconia, vanadium recovery; hybrid oxide materials, harmful metal ions

1. Introduction

In the era of constant development of civilization and industry, the demand for innovative materials with unique properties increases. In recent years, the synthesis of hybrid oxide materials has enjoyed a great interest of scientific communities all around the world, due to the possibility of obtaining products with unique and specific physicochemical properties, which result in a wide range of their applications (Chen et al., 2014; Kurc et al., 2018; Kvisle et al., 1988; Marouka and Nanko, 2013; Pinho et al., 2013; Siwińska-Stefańska and Kurc, 2017; Song et al., 2014; Su et al., 2016; Sun et al., 2017; Wang et al., 2016). Such materials can be synthesized using already known techniques, such as hydrothermal method, electrochemical method, in-situ synthesis, as well as the sol-gel method. In order to improve physicochemical properties, these systems can be further modified by variety of ways, e.g. by doping, chemical modification, immobilization, electrophoretic deposition or the introduction of metal ions by in situ synthesis.

Compared to other methods, the sol-gel technique has many advantages, including the ability to accurately control the surface area and pore volume, as well as the possibility to synthesize materials with a micro- and nanostructure characterized by high purity (Tyagi et al., 2006). The sol-gel method is based on successive hydrolysis and condensation reactions, which lead to the formation of a metal oxygen-metal (-Me-O-Me-) bridge (Sakka, 2013). The basic substrates are metal alkoxides and the hydrolysis promoter – a strongly acidic or basic solution, of which the traditionally used are hydrochloric acid and ammonia. The type of used hydrolysis promoter affects the physicochemical properties of the final product, such as morphology or porous structure. The specificity of the sol-gel method allows its easy modification and trouble-free introduction of dopant into the structure of the final material via in situ synthesis.

Nowadays, the sol-gel technique is one of the most popular methods for the synthesis of inorganic oxide materials, such as zirconium dioxide (Sakka, 2013). Zirconia is a material with good electrical, mechanical and biological properties (Bashir et al., 2013). Due to its microstructural properties (the crystalline phase, the shape and size of particles) it is widely used in industry (Madhusudhana et al., 2006). Zirconia is also an important material used in composites and advanced ceramic materials due to its high strength, crushing resistance and hardness (Bashir et al., 2013). These properties can be improved by incorporating various dopants such as gold, silver, nickel, platinum, copper, zinc or vanadium. The incorporation of vanadium species in the structure of zirconia should increase the dielectric constant and improve the ferroelectric properties (Padmamalini and Ambujam, 2014), as well as improve its thermal and optical properties (Albrecht et al., 1997). In addition, vanadium ions reduce the energy gap, and thus improve photocatalytic activity in the near UV range (Assem and Oskarsson, 2015), and increase the electric capacity and conductivity of the material. Materials enriched with vanadium are used, among others, as porous lithium-ion battery electrodes, in photocatalysis processes and the production of supercapacitors.

Vanadium is widely applied in industries such as metallurgy, mining, oil refining, automobile, and many others (Sharififard et al., 2016; Omidinasab et al., 2018). Such a wide range of applications results in the formation of significant amount of sewage contaminated with vanadium, which in the final stage end up in environmental waters. Due to the need to use of this element in many areas of industry and the difficulty of obtaining it, recovery from wastewater seems to be an interesting alternative. Thus, in this work, the possibility of usage of alkaline solutions contaminated with vanadium as a hydrolysis promoter in the synthesis of ZrO₂/V hybrid systems via modified sol-gel route was examined. The research cycle was divided into three sequences: (1) checking how the change of the hydrolysis promoter from ammonia to NaOH solution affects the properties of the obtained zirconium dioxide, (2) examination whether NaOH solutions contaminated with vanadium ions can be used as a hydrolysis promoter and how the presence of vanadium affects the properties of the obtained materials, (3) checking whether real waste solutions formed after vanadium catalyst leaching can be used as a hydrolysis promoter in the synthesis of ZrO₂/V systems and how the presence of other impurities in the sewage affects the properties of final materials.

2. Materials and methods

2.1. Reagents and materials

Zirconium tetraisopropoxide (70 wt. % in 1-propanol), used as a zirconium promoter was ordered from Sigma-Aldrich. Ammonia (25% solution) and dilution of sodium hydroxide (20% solution), used as hydrolysis promoters, originated from Chempur. Propan-2-ol (≥99.0%), which was used as the synthesis medium, was obtained from Chempur. Sodium metavanadate (≥98.0%), which solutions were used as model metal precursors in modified synthesis route, was ordered from Sigma-Aldrich. Potassium bromide (FT-IR grade, ≥99%), originating from Sigma-Aldrich, was used in preparation of tablets for FT-IR analysis. The solutions after leaching of the used vanadium catalyst were real vanadium solutions.

2.2. Sol-gel synthesis and characterization of obtained materials

Zirconium(IV) oxide was synthesized via sol-gel route. Appropriate volume of propan-2-ol was placed into reaction vessel and then zirconium tetraisopropoxide (TZIP) was dosed using peristaltic pump.

The system was stirred for half hour. Next, the promoter of hydrolysis, the NaOH solution, was dosed and whole system was stirred for one hour. In case of obtaining hybrid materials model and real waste solutions containing vanadium ions were used as hydrolysis promoters. Then the system was poured into crystallizer and left for gelation for approximately 48 h. After aging process, material was dried in 80°C within 24 h. Then it was washed with deionized water, once again dried in Memmert drying oven in the air atmosphere, grinded and sieved through 80 µm sieve. All experiments were carried out at room temperature and open atmosphere.

Obtained materials were subjected to physicochemical analysis using scanning electron microscopy (SEM), dynamic light scattering (DLS), energy-dispersive X-ray microanalysis (EDS), Fourier transform infrared spectroscopy (FT-IR), low-temperature nitrogen sorption (BET), thermogravimetric analysis (TGA).

3. Results and discussion

3.1. Optimization of the ZrO₂ synthesis process

In the initial stage of research, optimization of the zirconia synthesis using sodium hydroxide solutions as a hydrolysis promoter was carried out. The use of sodium hydroxide is due to the fact that it is more often used in industry than ammonia. NaOH solutions with concentrations of 5, 10, 15 and 20% were used. The synthesis course was compared with the previously optimized process of obtaining zirconia with the use of 25% ammonia as hydrolysis promoter. In the processes, where 15 and 20% NaOH solutions were used as hydrolysis promoters, the gelation of the samples was observed already during the dosing. Such phenomenon is unfavorable, due to the formation of aggregates, which results in a non-homogeneous structure of the obtained material. Syntheses proceeded using lower concentrations of NaOH were flawless. Due to the desire to limit the amount of water introduced into the system, it was found that the most favorable concentration of sodium hydroxide is 10%.

3.2. Comparison of physicochemical properties of ZrO₂ obtained using various basic hydrolysis promoters

The results of the analysis proved that samples synthesized using different hydrolysis promoters do not differ significantly. The comparison of porous structure parameters and surface composition of the obtained materials are summarized in Table 1. Both samples have a relatively high surface area oscillating around 140 m²/g, and the average pore size smaller than 7 nm. The BET isotherms for the obtained oxides are shown in Fig. 1. Their course indicates that they are type II isotherms, characteristic for macroporous and non-porous materials. The absence of a hysteresis loop does not allow to talk about mesoporosity of those materials, as it is indicated by the average pore size. High concentration of zirconium and oxygen was observed in both materials, which indirectly confirms the efficiency of ZrO₂ creation. Signals from nitrogen and sodium may occur, due to the presence of impurities originating from the hydrolysis promoters and the reaction environment, which was air.

The FT-IR spectra obtained for ZrO₂ synthesized with the use of 10% NaOH and 25% NH₃ as hydrolysis promoters are shown in Fig. 2. Analyzing the spectra in the wavelength range 3570-3200 cm⁻¹ a wide band corresponding the stretching modes of OH bands related to free water (surface adsorbed water) (Coates, 2006; Dou et al., 2012) can be noticed for both samples. Maxima of that bands

Table 1. Comparison of physicochemical properties of zirconia obtained using different hydrolysis promoters

	ZrO ₂ (NaOH)	ZrO ₂ (NH ₃)
Structure	amorphous	amorphous
BET surface area (m ² /g)	145	141
Average pore size (nm)	6.9	6.7
Average pore volume (cm ³ /g)	0.11	0.11
Zirconium content (wt.%)	56.5	59.6
Oxygen content (wt.%)	37.5	37.7
Sodium content (wt.%)	4.0	2.7
Nitrogen content (wt.%)	2.0	0.1

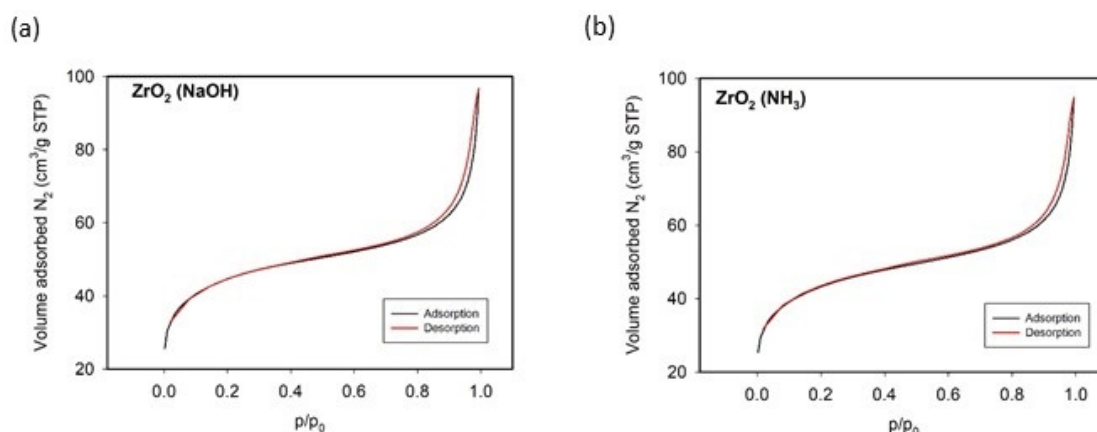


Fig. 1. The BET adsorption-desorption isotherms of zirconia obtained using a) NaOH and b) NH_3 as hydrolysis promoter

are located at 3413 cm^{-1} and 3367 cm^{-1} for the sample obtained with the use of NaOH and ammonia, respectively. The bands located between 1367 and 1353 cm^{-1} are assigned to the stretching vibrations of the Zr-OH moieties (Liu et al., 2008; Sarkar et al., 2007; Simmons, 1992; Toullec et al., 1988), while the bands with a maximum in the range of 815 - 793 cm^{-1} are derived from the stretching vibrations of Zr-O (Patel et al., 2017). The FT-IR spectra of the tested systems differ only in intensity - in both samples, signals from the Zr-O and Zr-OH groups were recorded, as well as a signal from the O-H binding. No shifts in the wavenumber range were observed, suggesting that ZrO_2 obtained using NaOH is chemically identical to ZrO_2 obtained with NH_3 .

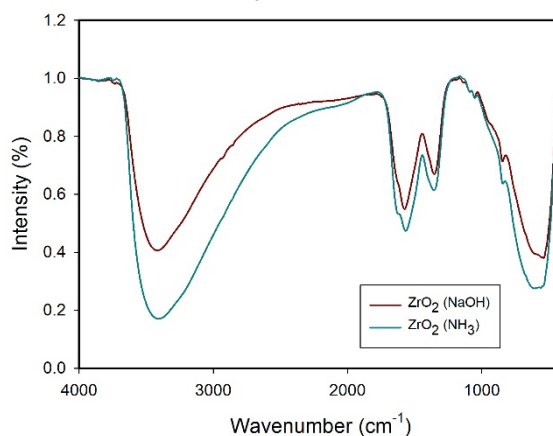


Fig. 2. The FT-IR spectra of ZrO_2 obtained using different hydrolysis promoters

Scanning electron microscopy (SEM) was used to determine the morphology, shape and size of individual grains of the synthesized materials. Analysis of the presented SEM images (Fig. 3) proves that the change of the hydrolysis promoter from NH_3 to NaOH did not significantly affect the morphology of the obtained oxides. In both cases particles of ZrO_2 are built of grains with different sizes and irregular shapes, which tend to agglomerate.

Zirconium(IV) oxides were tested for thermal stability and the TG curves are presented in Fig. 4. The samples lost about 25% of their mass when the temperature was below 400°C , which was probably related to the evaporation of water from the material structure and the partial degradation of the reagent residues after synthesis. The curve collapsed at around 700°C is clearly visible for the sample obtained using NaOH as the hydrolysis promoter. This may be a signal indicating the phase transformation of the ZrO_2 structure from amorphous to crystalline (Naguib and Kelly, 1970). After that the samples mass remained stable during heating. Considering that, it can be concluded that the oxides obtained are resistant to high temperatures, up to 1100°C .

In conclusion, both materials - obtained with the use of 25% NH_3 and 10% NaOH as the hydrolysis promoters - exhibit almost the same physicochemical properties. This proves that in this case the

chemical composition of the hydrolysis promoter used in sol-gel route does not significantly affect the properties of the ZrO_2 . In addition, it confirms the effectiveness of the modification of sol-gel method in the presented way.

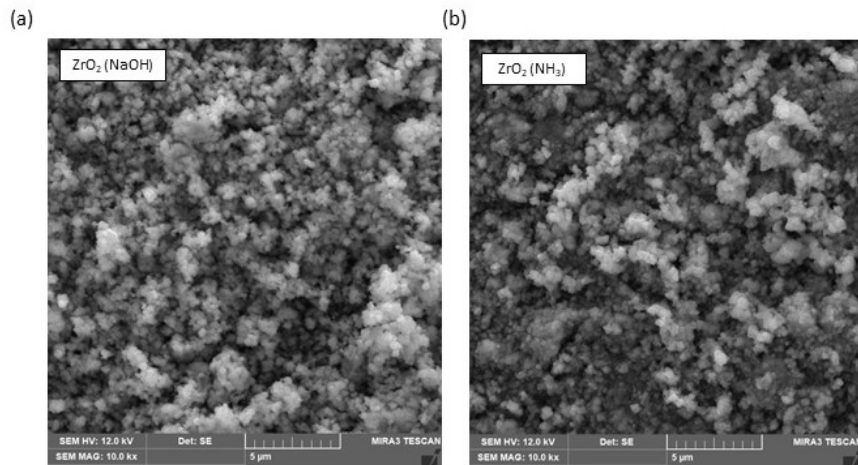


Fig. 3. The SEM images of ZrO_2 obtained via sol-gel route using a) NaOH and b) NH_3 as hydrolysis promoters

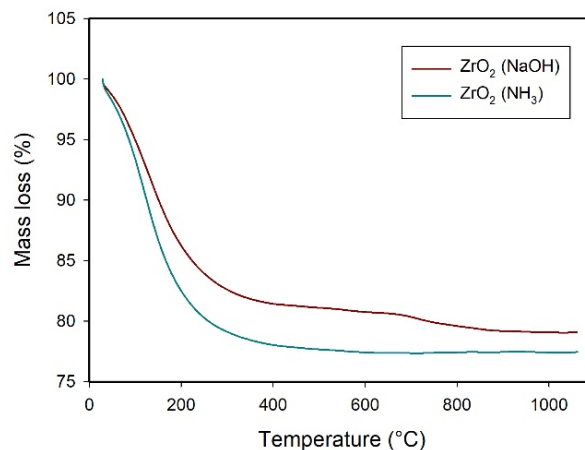


Fig. 4. Comparison of the TG curves of zirconia obtained with different hydrolysis promoters

3.3. Characterization of ZrO_2/V systems obtained with model vanadium solutions

The next stage of the research included an attempt to introduce vanadium ions into the zirconia structure. For this purpose, *in situ* sol-gel synthesis was carried out using NaOH and NH_3 solutions containing an appropriate concentration of vanadium ions as hydrolysis promoters. The samples were synthesized using the concentrations 10, 20, 50, 100 and 200 mg/dm^3 of vanadium ions in 10% NaOH and 25% ammonia.

The influence of the type of hydrolysis promoter on the final pH of the synthesis is shown in Fig. 5. As it can be seen, the final pH of the synthesis performed with the use of NaOH solutions (pH = 10-11) was higher when using NH_3 (pH = 8-10). In both cases, the pH increased as the vanadium ions were added to the solution.

The SEM analysis (Fig. 6) of model ZrO_2/V samples revealed irregular structure with various grain sizes and agglomeration tendency. The change of morphological features in the samples with vanadium additions were observed in comparison to pristine ZrO_2 samples. No tendency in change of grain size was observed with the increase of vanadium ions concentration regardless of the type of hydrolysis promoter used.

The particle-size distributions (PSD) of the obtained ZrO_2 and ZrO_2/V systems, shown in Fig. 7, were measured using dynamic light scattering (DLS) technique (Mastersizer 2000 instrument equipped with Hydro 2000 MU element). Detailed dispersive parameters of analysed samples are shown in Table 2

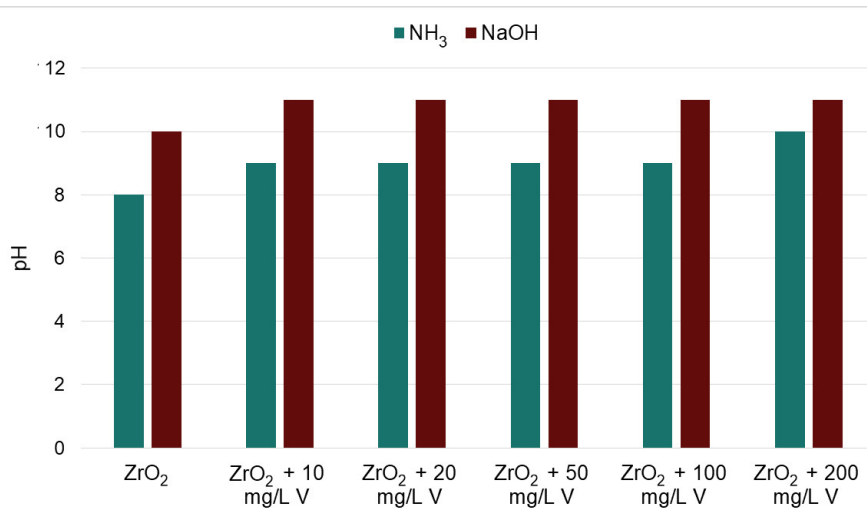
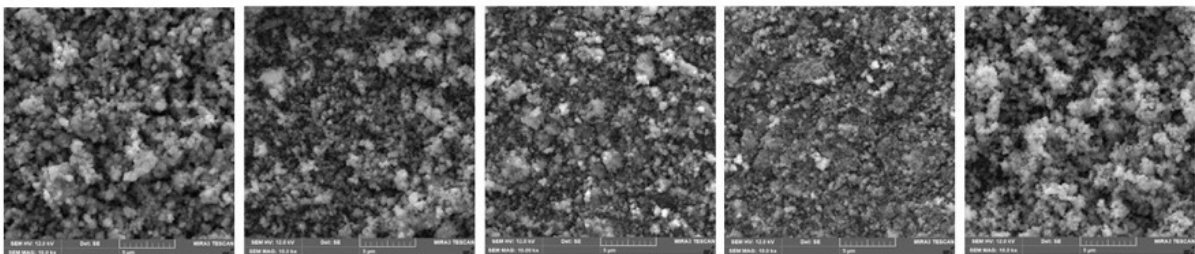


Fig. 5. Final pH of the synthesis processes performed using various hydrolysis promoters

(a) ZrO₂/V (NaOH)



(b) ZrO₂/V (NH₃)

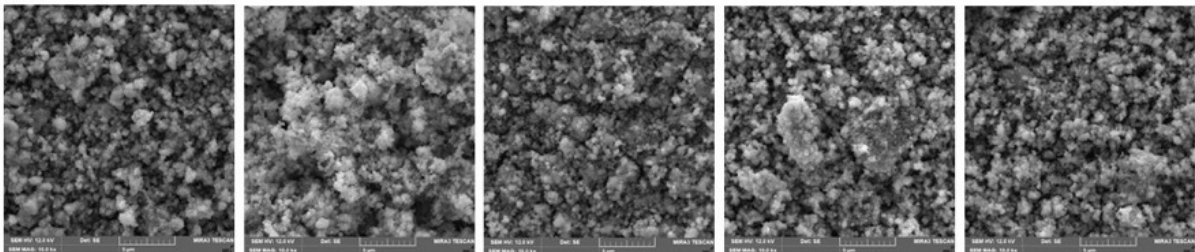


Fig. 6. SEM images of ZrO₂/V samples obtained with the use of 10, 20, 50, 100 and 200 mg/dm³ (from left to right) of vanadium ions dissolved in a) 10% NaOH or b) 25% NH₃ as hydrolysis promoters

provided data on the dispersion, grain size and agglomeration tendency of the obtained systems. By analyzing the data gathered in Table 2, a significant change in the dispersion characteristics of the obtained systems can be observed. In case of samples obtained using NaOH solutions as a hydrolysis promoter, a greater proportion of particles with a diameter below 2 μm was observed. All these materials showed the presence of 10% of particles of less than 1.2-1.8 μm, 50% of particles of less than 6.0-25.4 μm and 90% particles of less than 55.7-74.2 μm. Considering that the samples obtained with the use of ammonia showed higher values of the parameter $d(0.1)$ - 2.6-3.9 μm, their values of parameters $d(0.5)$ and $d(0.9)$ were lower reaching 9.3-15.0 and 39.0-62.5 μm, respectively. All vanadium-modified samples showed smaller average particle diameter than the reference samples, regardless of the type of used hydrolysis promoter. An improvement in dispersion parameters was observed with an increase in the addition of vanadium to the hydrolysis promoter. Nevertheless, its too high concentration, at the level of 200 mg/dm³, caused renewed decrease in this field. The best dispersion parameters were obtained for the sample ZrO₂ + 50 mg/dm³ V (NaOH), which showed the presence of 10% particles smaller than 1.5 μm, 50% particles smaller than 6.0 μm, 90% particles smaller than 55.7 μm, and its average particle size was 18.8 μm.

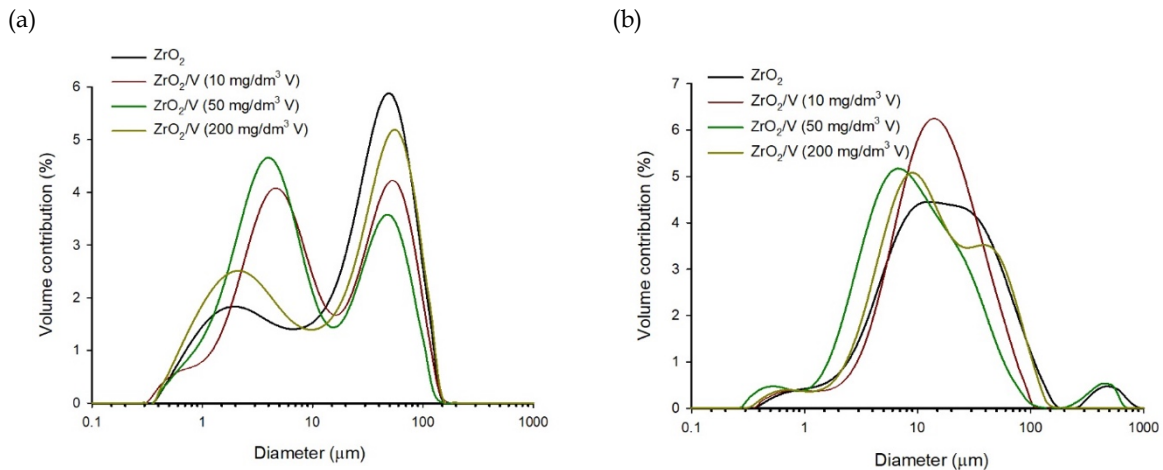


Fig. 7. PSD of ZrO_2/V samples obtained with the use of 10, 50 and 200 mg/dm^3 of vanadium ions dissolved in a) 10% NaOH or b) 25% NH_3 as hydrolysis promoters

Table 2. Dispersive parameters of ZrO_2/V samples obtained using NaOH and NH_3 as hydrolysis promoters

Sample	Hydrolysis promoter	Diameter (μm)			
		d(0.1)	d(0.5)	d(0.9)	D[4.3]
ZrO_2		1.4	25.4	72.2	31.1
$ZrO_2 + 10 mg/dm^3 V$	NaOH	1.8	9.3	65.8	24.0
$ZrO_2 + 50 mg/dm^3 V$		1.5	6.0	55.7	18.8
$ZrO_2 + 200 mg/dm^3 V$		1.2	19.7	74.2	29.3
ZrO_2		3.4	15.0	62.5	34.3
$ZrO_2 + 10 mg/dm^3 V$	NH_3	3.9	13.1	39.0	17.9
$ZrO_2 + 50 mg/dm^3 V$		2.6	9.3	39.6	26.5
$ZrO_2 + 200 mg/dm^3 V$		3.2	12.0	54.3	21.4

Similarly, to the pure ZrO_2 samples, FT-IR spectra of ZrO_2/V systems (Fig. 8) exhibited signals from O-H ($3432-3367 cm^{-1}$), Zr-OH ($1367-1352 cm^{-1}$), Zr-O ($815-793 cm^{-1}$) stretching vibrations. Moreover, the bands at about 1364 and $903 cm^{-1}$ can also indicate Zr-O-V stretching vibrations (Rasheed et al., 2020). In addition, in the wavelength range of $606-530 cm^{-1}$ signals from V-O-V bending vibrations are observed for all samples modified with vanadium (Rasheed et al., 2020). The identified bands of groups on the surface of the material indirectly confirm the effective synthesis of zirconia. In addition, based on the observation of signals derived from Zr-O-V bending vibrations in modified samples, the effectiveness of incorporating vanadium into the structure of zirconium(IV) oxide can be indirectly confirmed.

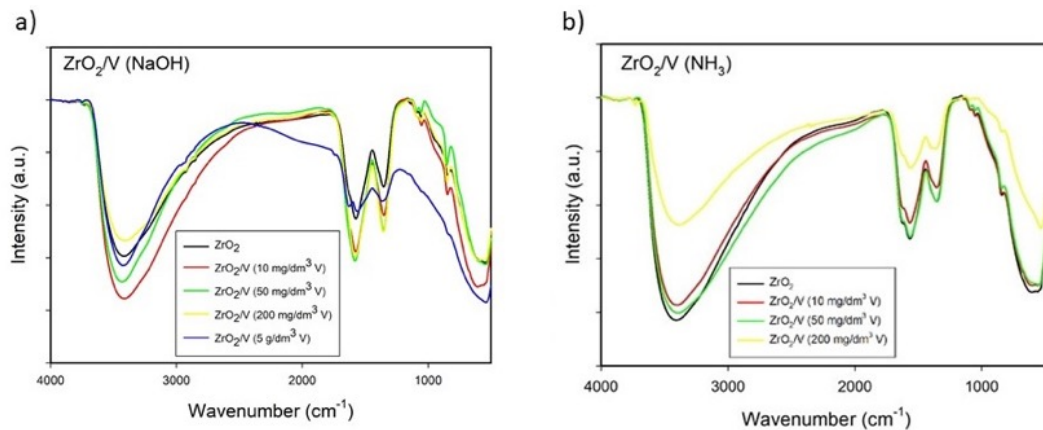


Fig. 8. The FT-IR spectra of ZrO_2/V obtained by sol-gel method with different hydrolysis promoters: a) 10% NaOH and b) 25% NH_3

Table 3 summarizes the results of EDS analysis for all synthesized samples of oxide materials enriched with vanadium in NaOH solution environment. All of the obtained samples are mostly composed of oxygen and zirconium. The percentage content of zirconium varies between 47 and 68%, while oxygen accounts for 37-45%. This fact may be an indirect confirmation of the effectiveness of the zirconia synthesis. Analyzing the data presented in Table 3, it can be seen that with an increase of vanadium concentration in the NaOH precursor, the percentage of zirconium in the final sample decreases. The presence of nitrogen can be caused by the use of 25% ammonia as a hydrolysis promoter, as well as by contaminations belonging from reaction environment. In addition, in samples obtained with the use of NaOH solution as a hydrolysis promoter a sodium content of 2.0-5.1% was observed. Vanadium signals were recorded on the EDS spectrum only for sample, for synthesis of which a solution containing 5 g/dm³ vanadium ions was used as the hydrolysis promoter. However, the presence of vanadium was not recorded in the percentage composition of most of the samples, but the signal from vanadium is clearly visible in the photos from the sample surface mapping (Fig. 9-10). This phenomenon may occur due to the fact that vanadium and oxygen have very similar keV values (vanadium - 0.511, oxygen - 0.525) and due to the very low intensity of vanadium bands, as well as the fact that the intense oxygen signal can mask the signal from vanadium in this analysis.

Table 3. The results of EDS analysis for ZrO₂/V samples obtained at various synthesis conditions

Sample	Hydrolysis promoter	Element content (wt.%)				
		Zr	O	N	Na	V
ZrO ₂ + 10 mg/dm ³ V	NaOH	58.2	37.3	1.8	2.5	0.0
ZrO ₂ + 20 mg/dm ³ V		54.0	41.3	2.5	2.2	0.0
ZrO ₂ + 50 mg/dm ³ V		49.2	45.2	0.8	4.7	0.0
ZrO ₂ + 100 mg/dm ³ V		48.0	47.3	0.8	3.9	0.0
ZrO ₂ + 200 mg/dm ³ V		52.7	40.4	1.1	5.8	0.0
ZrO₂ + 5 g/dm³ V		67.7	31.8	-	0.1	0.4
ZrO ₂ + 10 mg/dm ³ V	NH ₃	59.9	37.6	2.4	0.0	0.0
ZrO ₂ + 20 mg/dm ³ V		60.1	38.0	1.9	0.0	0.0
ZrO ₂ + 50 mg/dm ³ V		60.1	37.3	2.6	0.0	0.0
ZrO ₂ + 100 mg/dm ³ V		57.8	40.0	2.2	0.0	0.0
ZrO ₂ + 200 mg/dm ³ V		60.9	37.7	1.4	0.0	0.0

All of the obtained hybrid materials have a relatively large surface area, oscillating in the range of 137-232 m²/g. The highest surface area was obtained for the ZrO₂/V obtained with 200 mg/dm³ of vanadium ions in 10% NaOH as a hydrolysis promoter. Analyzing the data from Table 4, it can be seen that with an increase of vanadium content in NaOH solution, the surface area of the final ZrO₂/V material increases. The use of the promoter with the 200 mg/dm³ of vanadium ions, causes an increase of 88 m²/g of surface area when compared to the sample obtained with pure NaOH solution. In case of

Table 4. The porous structure data for ZrO₂/V obtained at various synthesis conditions

Sample	Hydrolysis promoter	BET surface area (m ² /g)	Average pore size (nm)	Average pore volume (m ³ /g)
ZrO ₂		145	6.9	0.11
ZrO ₂ + 10 mg/dm ³ V	NaOH	152	2.2	0.07
ZrO ₂ + 50 mg/dm ³ V		213	2.1	0.05
ZrO ₂ + 200 mg/dm ³ V		233	7.8	0.12
ZrO₂ + 5 g/dm³ V		224	5.1	0.21
ZrO ₂	NH ₃	141	6.7	0.11
ZrO ₂ + 10 mg/dm ³ V		175	7.6	0.10
ZrO ₂ + 50 mg/dm ³ V		140	2.2	0.05
ZrO ₂ + 200 mg/dm ³ V		138	2.1	0.03

using ammonia as hydrolysis promoter no such tendency was observed – the surface area of obtained ZrO_2/V hybrids was almost constant. The average pore size of all samples oscillated in the range of 2-8 nm. In Fig. 11 BET adsorption-desorption isotherm for $\text{ZrO}_2 + 5 \text{ g/dm}^3 \text{ V}$ system was presented. It can be seen that the course of this isotherm is almost the same as for pristine zirconia.

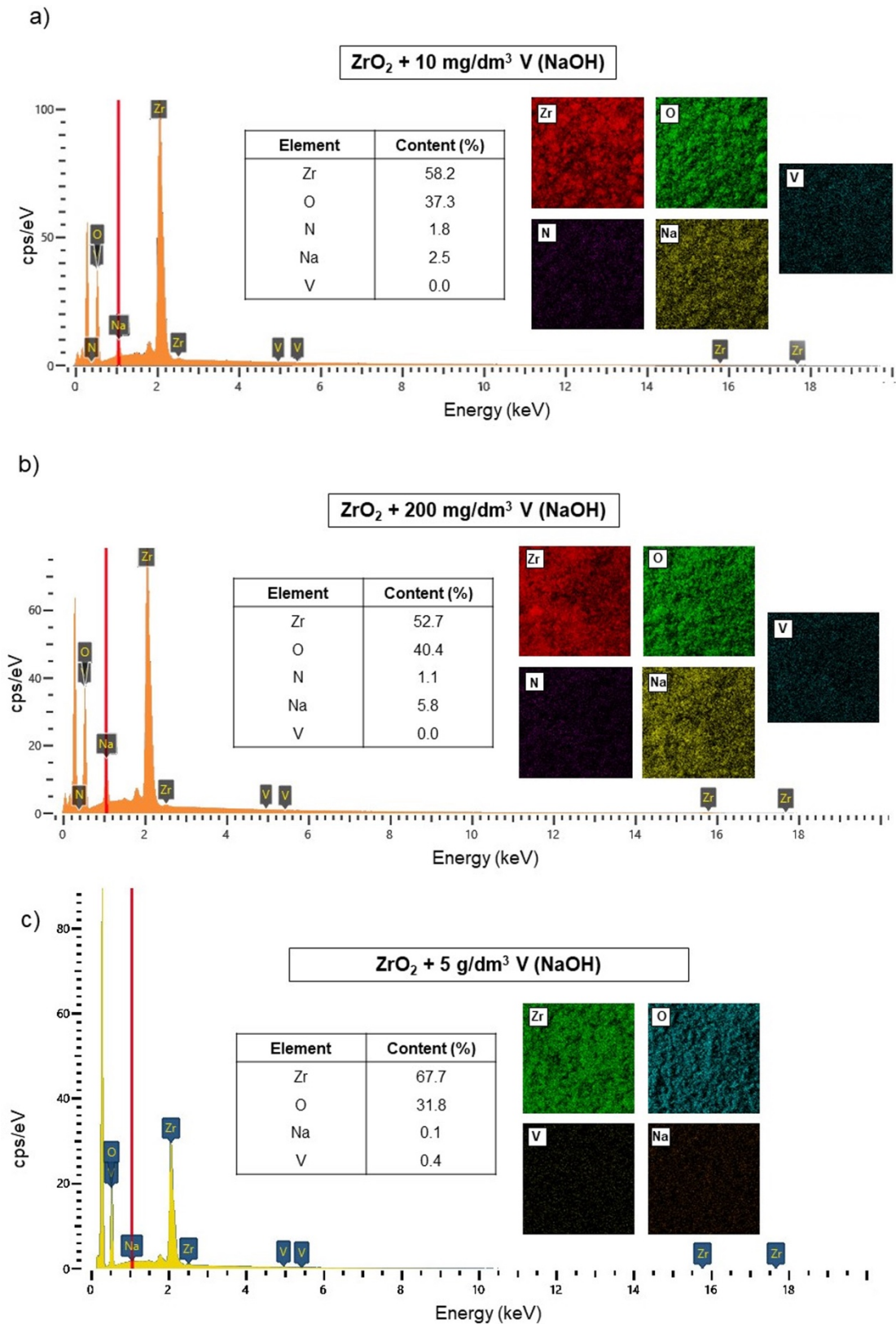


Fig. 9. EDS spectra with surface mapping for ZrO_2/V system synthesized by the use of a) 10 mg/dm^3 , b) 200 mg/dm^3 and c) 5000 mg/dm^3 vanadium ions in 10% NaOH solution

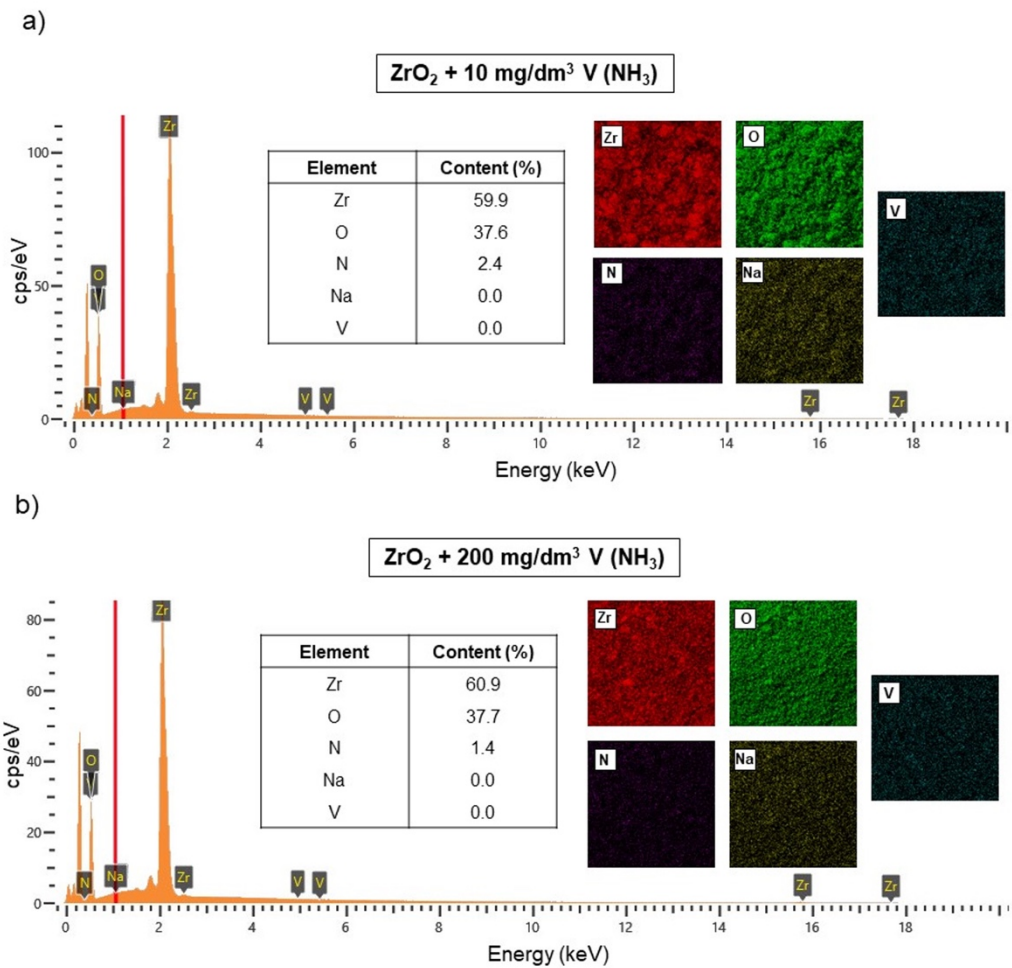


Fig. 10. The EDS spectra with surface mapping for ZrO₂/V system synthesized by the use of a) 10 mg/dm³ and b) 200 mg/dm³ vanadium ions in 25% NH₃ solution

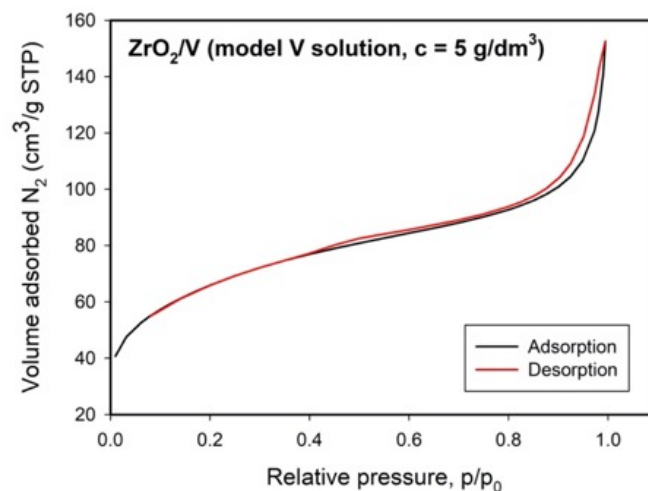


Fig. 11. The BET adsorption-desorption isotherm for ZrO₂/V obtained using model vanadium solution (c = 5 g/dm³, 10% NaOH)

3.4. Characterization of ZrO₂/V systems obtained with real vanadium solutions

Next stage of the research was the application of real vanadium solutions as hydrolysis promoters in synthesis of ZrO₂/V systems. For this purpose, the solution formed after leaching of vanadium catalyst

with 15% sodium hydroxide solution was used. Exact content of elements in the raw real vanadium solutions is presented in Table 5. In the role of hydrolysis promoters, the raw real solution and its dilution of 10 and 200 mg/dm³ were used.

Table 5. The composition of real wastewater originating from leaching of the vanadium catalyst

Element	Concentrations (mg/dm ³)
V	4953
K	11.33
Fe	0.0192
Na	93.33
S	8.636
Cl	not detected
Si	0.9377
Cu	0.6

SEM photographs of materials synthesized using real vanadium wastewater solutions are shown in Fig. 12. Similarly, to the materials discussed earlier, particles with irregular distribution and tendency to agglomeration were observed. However, compared to their counterparts obtained using model solutions, a more spherical and evenly distributed grain size can be observed.

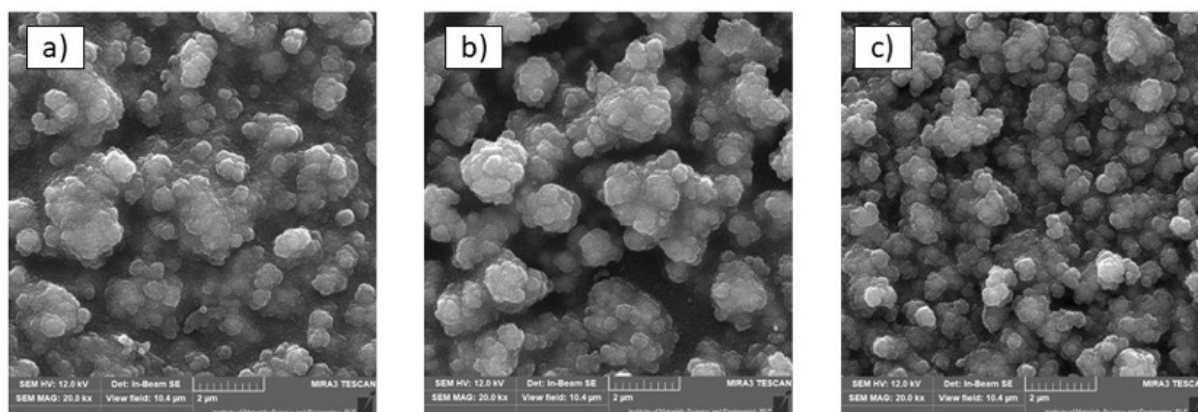


Fig 12. SEM images of ZrO₂/V samples obtained with the use of real vanadium wastewater in concentration of a) 10 mg/dm³, b) 200 mg/dm³ and c) 4953 mg/dm³ (real) with respect to vanadium ions

The PSD of ZrO₂/V samples obtained with the use of real vanadium wastewater is shown in Fig. 13, while detailed dispersive parameters are placed in Table 6. In comparison with ZrO₂/V systems obtained with the use of model vanadium solutions as hydrolysis promoters, the samples obtained with the use of real vanadium wastewater revealed similar or even slightly better dispersion parameters. These systems are characterized by a lower average particle diameter and a higher proportion of particles with smaller sizes. Again, an improvement in dispersion properties was observed with increasing vanadium concentration in the hydrolysis promoter, however this time they have not been deteriorated beyond a V concentration of 200 mg/dm³. Interestingly, the best dispersion parameters were obtained for sample synthesized with the use of prisitne sewage, where 10% of particles did not exceed 1.5 μm, 50% - 5.8 μm and 90% - 61.1 μm, while its average diameter is equal to 19.9 μm. This may be caused due to the presence of pollutants in the real sewage and their influence on the particle formation during synthesis.

Analyzing the FT-IR spectra (Fig. 14) the signals from analogous groups as in the case of raw ZrO₂ and ZrO₂/V systems obtained using model solutions can be observed. The bands corresponding to the observed signals from O-H, Zr-OH, Zr-O stretching vibrations and Zr-O-V and V-O-V bending vibrations are also observed in this way. This is an indirect confirmation of the effectiveness of the use of waste solutions containing vanadium compounds as a hydrolysis promoter in the synthesis of ZrO₂/V by the modified sol-gel method.

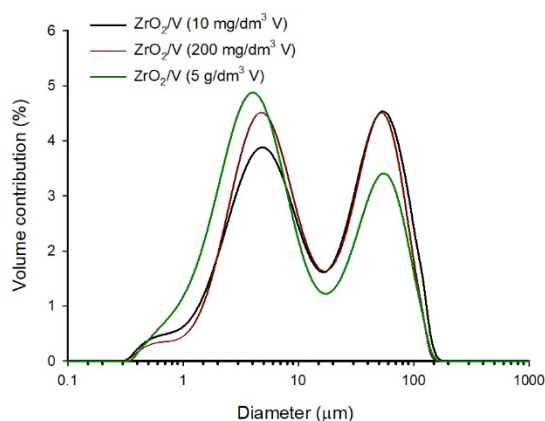


Fig. 13. PSD of ZrO_2/V samples obtained with the use of real vanadium wastewater in concentration of a) 10 mg/dm³, b) 200 mg/dm³ and c) 4953 mg/dm³ (real) with respect to vanadium ions

Table 6. Dispersive parameters of ZrO_2/V samples obtained using real vanadium wastewater

Sample	Diameter (μm)			
	d(0.1)	d(0.5)	d(0.9)	D[4.3]
$ZrO_2 + 10 \text{ mg/dm}^3 \text{ V}$	2.0	11.7	71.4	26.9
$ZrO_2 + 200 \text{ mg/dm}^3 \text{ V}$	2.2	9.5	64.8	24.1
$ZrO_2 + 5 \text{ g/dm}^3 \text{ V}$	1.5	5.8	61.1	19.9

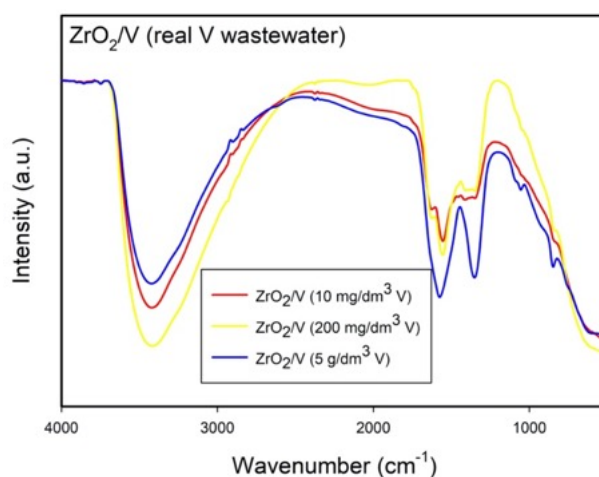


Fig. 14. The FT-IR spectra of ZrO_2/V obtained by sol-gel method with different dilution of real vanadium contaminated wastewater used as hydrolysis promoters

This fact is also confirmed by the EDS analysis results. The spectra along with the surface mapping are shown in Fig. 15. The zirconium content ranges from 58 to 69 wt.%, while oxygen from 30 to 37 wt.%. Together with the results of the FT-IR analysis it can be an indirect confirmation that the main building material of the obtained material is zirconium dioxide. Vanadium content was observed for both ZrO_2/V systems synthesized with the use of raw vanadium wastewater as well its dilution containing 200 mg/dm³ of vanadium ions. For the material synthesized using a concentrated scrubber after vanadium catalyst leaching, the vanadium content was at the level of almost one percent by mass. Sodium contamination of sewage did not significantly affect the elemental composition of the obtained materials.

The results of the BET analysis collected for samples obtained using real solutions are shown in Table 7. A significant decrease in the value of the surface area of the obtained materials is noticeable, in comparison to the pristine oxide material and hybrids obtained using model vanadium solutions. Also, when real waste solutions are used, a significant decrease in the surface value is observed with

increasing vanadium concentration. It can be concluded that too high concentration of vanadium ions in the solution used as a hydrolysis precursor helps to reduce the surface area of the final product.

Table 7. The porous structure data obtained for ZrO_2/V synthesized using different dilutions of real vanadium wastewater as hydrolysis promoters in the sol-gel synthesis

Sample	BET surface area (m^2/g)	Average pore size (nm)	Average pore volume (m^3/g)
$ZrO_2 + 10 \text{ mg/dm}^3 \text{ V}$	231	4.4	0.17
$ZrO_2 + 200 \text{ mg/dm}^3 \text{ V}$	247	4.3	0.19
$ZrO_2 + 5 \text{ g/dm}^3 \text{ V}$	100	4.7	0.12

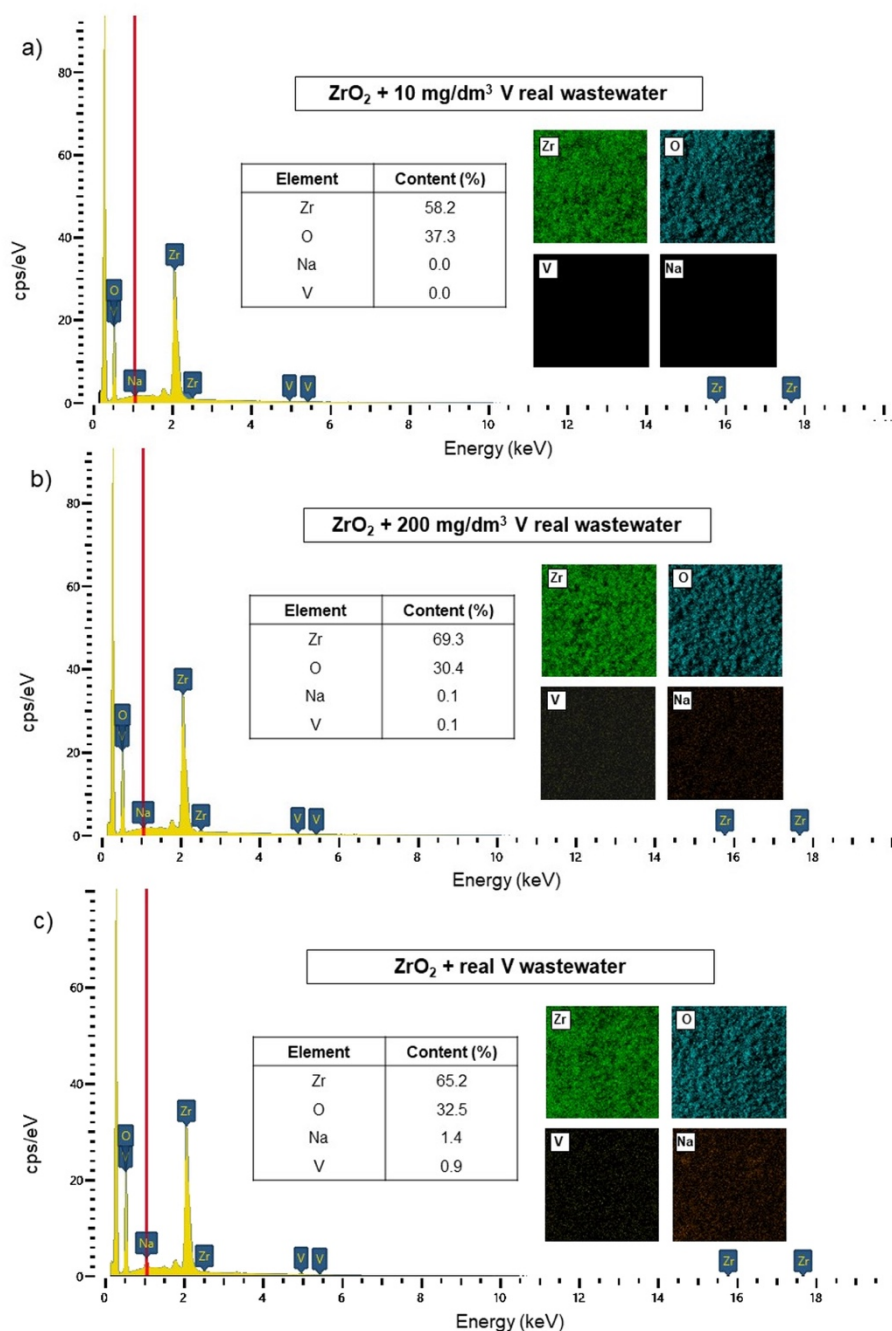


Fig. 15. The EDS spectra with surface mapping obtained for ZrO_2/V systems synthesized by the use of real vanadium wastewater, containing a) 10 mg/dm^3 , b) 200 mg/dm^3 and c) 4953 mg/dm^3 of vanadium ions

Fig. 16 presents the nitrogen adsorption-desorption isotherm obtained for a sample prepared using the crude solution after leaching of vanadium catalyst as a hydrolysis promoter of sol-gel synthesis. The course of the curve is similar to that obtained for pure ZrO_2 and for the ZrO_2/V hybrid synthesized using the model vanadium solution. However, due to the presence of the hysteresis loop, the obtained isotherm should be classified as type IV isotherm, not II as in the case of previous materials. Type IV isotherm is characteristic for mesoporous materials and suggests a multilayer adsorption mechanism followed by capillary condensation (Kruk and Jaroniec, 2001). The presence of the hysteresis loop is associated with capillary condensation taking place in the mesopores, and the limiting uptake over a range of high p/p_0 (Sing et al., 1985). Type 4 hysteresis loop is clearly visible on the isotherm, which indicates the presence of narrow slit-like pores, as well as particles with internal voids of irregular shape and broad size distribution. The analysis of these results leads to the conclusion that the use of a real wastewater solution containing vanadium ions with a concentration of 4953 mg/dm^3 as a hydrolysis promoter in the ZrO_2/V synthesis process by the modified sol-gel method contributes to the improvement of nitrogen sorption ability, despite the decrease in surface of the material. This may be due to the presence of active functional groups.

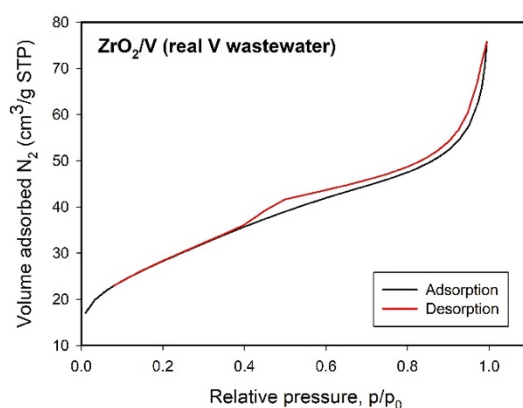


Fig. 16. BET adsorption-desorption isotherm of ZrO_2/V obtained using real vanadium wastewater ($c = 4953 \text{ mg of V/dm}^3$)

4. Conclusions

Zirconia and ZrO_2 oxide systems enriched with vanadium were synthesized using a modified sol-gel method. The variable parameter was the type of basic precursor and vanadium concentration to select the most favorable conditions. It has been shown that the type of the basic precursor does not significantly affect the chemical composition of the ZrO_2 . All of the obtained materials were characterized by particles of various sizes and irregular shapes, which tend to agglomerate. Vanadium incorporation was indirectly confirmed by the presence of vanadium signals in the EDS mapping photos and the presence of Zr-O-V vibrations in the FT-IR spectrum of all ZrO_2/V samples obtained with model vanadium solutions as hydrolysis promoters. It has been observed that, with an increase in vanadium concentration in NaOH solutions used as hydrolysis promoters, the surface area of the materials increases significantly, while for the 25% ammonia no such trend was observed. The highest surface area ($233 \text{ m}^2/\text{g}$) was observed for ZrO_2 modified with 200 mg/dm^3 of vanadium in a 10% NaOH solution environment. It has been confirmed that using the real solution, obtained as a result of vanadium catalyst leaching, through the sol-gel process, it is possible to obtain a mesoporous hybrid ZrO_2/V material. The incorporation of vanadium into its structure was confirmed by the results of both FT-IR and EDS analyzes. The effective use of raw sewage in the sol-gel synthesis process gives a chance for its application as a hydrolysis promoter in sol-gel synthesis processes. This is of great importance for the elimination of such pollutants from the environment, in a process that will also produce multifunctional hybrids.

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