



Quantitative LIBS analysis of vanadium in samples of hexagonal mesoporous silica catalysts

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ABSTRACT

The method for the analysis of vanadium in hexagonal mesoporous silica (V-HMS) catalysts using Laser Induced Breakdown Spectrometry (LIBS) was suggested. Commercially available LIBS spectrometer was calibrated with the aid of authentic V-HMS samples previously analyzed by ICP OES after microwave digestion. Deposition of the sample on the surface of adhesive tape was adopted as a sample preparation method. Strong matrix effect connected with the catalyst preparation technique (1st vanadium added in the process of HMS synthesis, 2nd already synthesised silica matrix was impregnated by vanadium) was observed. The concentration range of V in the set of nine calibration standards was 1.3–4.5% (w/w). Limit of detection was 0.13% (w/w) and it was calculated as a triple standard deviation from five replicated determinations of vanadium in the real sample with a very low vanadium concentration. Comparable results of LIBS and ED XRF were obtained if the same set of standards was used for calibration of both methods and vanadium was measured in the same type of real samples. LIBS calibration constructed using V-HMS-impregnated samples failed for measuring of V-HMS-synthesized samples. LIBS measurements seem to be strongly influenced with different chemical forms of vanadium in impregnated and synthesised samples. The combination of LIBS and ED XRF is able to provide new information about measured samples (in our case for example about procedure of catalyst preparation).

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1. Introduction

Hexagonal mesoporous silica (HMS) belongs to a group of mesoporous molecular sieves [1]. These materials are characteristic with a high specific surface area ($700\text{--}1500\text{ m}^2\text{ g}^{-1}$), large specific pore volume, highly organized porous structure, narrow pore size distribution, high thermal stability and chemical resistance. Great attention has been focused on these materials as catalysts support. For example, vanadium species supported on HMS exhibited high activity in selective oxidation of hydrocarbons.

Analysis of total vanadium content in V-based catalysts belongs to an integral part of its characterization process [2]. Conventional methods of the elemental analysis requiring sample in the form of solution (AAS, ICP OES) suffer with a wide range of complications connected with sample preparation process. High pressure decomposition of samples in corrosive chemicals (HF, aqua regia) or fusion is necessary to transfer analyte into the solution. Sample consumption is often unsatisfactory for these procedures. Thus

several practical and economic reasons invoke the current trend towards fast and nondestructive methods. Analysis of vanadium in silica catalysts seems to be a typical application area for spectral techniques enabling direct elemental analysis of solid samples like XRF or LIBS.

Selection of appropriate sample preparation technique is also important step during the optimization of LIBS method. Powdered samples are usually pressed to the pellets or deposited on the surface of adhesive tape.

Pressing pellets was already used for quantitative elemental LIBS analysis of soils [3,4], cryogenically ground plant tissues [5,6], coal [7], thorium–uranium oxides [8] and tungsten carbides [9]. Gondal et al. performed a detailed study of various binding materials (potassium bromide, polyvinyl-alcohol, starch, silver and aluminum) in application for elemental analysis of trace contaminants in powdered Mg [10]. The study revealed that the binding material strongly influences ablated sample masses as well as depths and profiles of originated craters and plays an important role in the generation of LIBS signal.

Deposition of powder sample on surface of adhesive tape is well described for example by Tran et al., who compared pellet pressing and sample deposition on adhesive tape for analysis of trace met-

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als (Mn, Co, Fe, and Na) in terephthalic acid [11]. However, values of signal-background ratio were better for on tape samples. Thus, limits of detection ($0.2\text{--}2\text{ mg kg}^{-1}$) as well as accuracy ($1\text{--}5\%$) were very similar for both sampling methods.

On tape sample deposition together with pellet preparation were also used by Ctvrtnickova et al. as sample preparation methods for LIBS characterization of fly ash [12]. Pressed pellets were prepared with three different binders – wax, KBr and polyvinyl alcohol (PVA). In the case of “on tape” deposition, the powdered sample was stuck as a uniform layer on a carbon double-side-adhesive tape. By authors statement, the time of pellet preparation including weighing, homogenizing and pressing was about 5 min, while samples mixed with PVA were prepared in about 22 min and “on tape” sticking took no more than few seconds. High carbon content presented in tape base prevented application of this sample preparation method for purposes of quantitative analysis of carbon.

Quantitative analysis of Ce, Cr, Si, Fe, Ta, Ni, Zn, Al Mg, Gd, and W in CeO_2 composite powder using laser-induced breakdown spectroscopy was performed by Zheng et al. [13]. Samples were prepared in the form of pellets using PVA (2%) as a binder and in the powder form by adhering one thin layer of particles to double sided tape mounted on a microscope slide. The accuracy and precision of the LIBS results were better than 5% for the major elements and better than 10% for most of the minor elements. It was concluded, that the pellet data gave slightly better precision than the powder sample.

On tape powder deposition was described by Anzano et al. [14] too. It effectively reduces the matrix effects in LIBS analysis of geological samples. Synthetic model samples prepared from various iron and aluminum compounds spiked with SiO_2 and CaCO_3 matrices were analyzed in either the powder or pressed pellet forms. More accurate concentrations were determined from only those samples prepared as powders (typical errors of 5.6% for Al_2O_3 and 0.3% for SiO_2), indicating the absence of matrix effects that are typically observed. Experimental results agreed well with certified values only for on tape deposited samples with particle size greater than $100\text{ }\mu\text{m}$.

Adhesive tape pressed against the skin was used by Rosenberg and Dockery for collection of samples for purpose of gunshot residue testing [15]. Positive test for gunshot residue was defined when the barium 455.403 nm emission line produced signal minus background emission values greater than the calculated signal detection limit at any location along the sample tape.

The main aim of our work was to develop a fast, cheap, and effective methodology for the analysis of vanadium in mesoporous silica catalysts using laser induced breakdown spectroscopy. HMS samples were not possible to press into pellets without substantial addition of appropriate binder. To avoid complications connected with pellets creation (difficulty of binder selection, high sample consumption, possible sample contamination, etc.) it was decided to adopt the powder deposition on surface of the adhesive tape as a sample preparation method.

2. Experimental

2.1. Preparation of HMS and V-HMS materials

Hexagonal mesoporous silica (HMS) was synthesized according to the procedure reported by Tanev and Pinnavaia [1]. HMS ($835\text{ m}^2\text{ g}^{-1}$) was prepared by dissolving 13.6 g dodecylamine (DDA, Aldrich) in the mixture of 144.6 ml ethanol and 200 ml re-distilled water (re- H_2O). After stirring for 20 min, 56 ml of tetraethylorthosilicate (TEOS, Aldrich) in 81 ml ethanol was added drop-wise and stirred. The synthesis was performed at $70\text{ }^\circ\text{C}$ for 18 h under static conditions. The solid product was filtered, washed with

re- H_2O and calcined in air at $450\text{ }^\circ\text{C}$ for 8 h. V-HMS based materials were prepared by two procedures. V-HMS-impr catalysts were prepared by impregnating HMS with solution of vanadyl acetylacetonate in ethanol. V-HMS-synt catalysts were prepared by the same procedure as pure HMS. Additionally, the solution of vanadyl acetylacetonate in ethanol was drop wise added to the synthetic gel [2,16]. Finally, V-HMS-impr and V-HMS-synt catalysts were pre-treated at $600\text{ }^\circ\text{C}$ in air for 8 h [2,16].

2.2. LIBS analysis

The LIBS spectrometer (LEA S500, Solar TII Ltd., Belarus) was used and it is fully described elsewhere [17]. The instrument has a dual pulse Q-switched Nd:YAG laser operating at 1064 nm . The laser emits two co-linear pulses of about 12 ns duration with energy per pulse typically variable between 80 and 150 mJ at a maximum repetition rate of 20 Hz. The inter-pulse delay can be set from 0 to 20 ms. The Czerny Turner spectrograph, with a focal length of 500 mm and grating of $1800\text{ lines mm}^{-1}$, provides a linear reciprocal dispersion of 1 nm mm^{-1} . The spectrograph is full sealed and can be purged by low flow of argon, so the wavelength range of the spectrograph is from 170 to 800 nm. Recording of the spectra is carried out by means of a back thinned and front illuminated CCD-camera (2048×14 pixels) with minimal integration time of 1 ms. Spectra are measured in arbitrary setting 30 nm regions. The samples are placed inside the sample chamber on the top of the motorized positioning table and the sample can be automatically moved during the analysis. Selection of analyzed area on sample surface is performed via inbuilt video system with factor of magnification 100 and is fully software controlled (position and number of points in pattern).

Samples of vanadium doped mesoporous silica were first diluted with pure HMS matrix in proportion 1:5 and then homogenized using ball vibration mill (model 3110-3A, Nicolet, USA). Dilution of samples by pure HMS matrix was used to uniform matrix effects connected with different types of measured V-HMS catalysts and also to enable using of Si line for normalizing of V analytical line. Fifty milligrams (50 mg) of V-HMS sample together with 250 mg of pure HMS matrix was accurately weighed to the capsule of vibration mil and then homogenized for 1 min with frequency 60 Hz. Obtained homogenous powder was then poured on the surface of adhesive tape with an area of $2\text{ cm} \times 3\text{ cm}$ and spread by soft brush. Nonintercepted part of sample was finally removed from tape surface by air flow.

2.3. ED XRF analysis

Desktop energy dispersive XRF spectrometer (Elva X, Elvatech Ltd., Ukraine) equipped with a Pd anode X-ray tube was used. Excitation X-ray beam was pre-treated by collimator (gap diameter 2 mm) and Ni filter. The tube was operated at 40 kV and $80\text{ }\mu\text{A}$. Thermoelectrically cooled solid state Si-pin detector with 5.5 mm^2 active area and $5\text{ }\mu\text{m}$ thick Be window was used. The resolution on Mn Ka line was better than 175 eV for 10,000 cps count rate. The spectrum collection live time was 100 s per analyzed sample. The instrument control, signal acquisition, spectrum treatment and quantitative analysis were carried out using Elvatech commercial software package. USB videocamera was used for accurate selection of analyzed part of sample. Integral intensity of V $\text{K}\alpha_1$ line with energy 4.95 keV was measured for purpose of calibration curve construction as well as for measurement of vanadium concentration in unknown samples. Homogenized mixture of V-HMS sample and pure HMS matrix was simply poured into the silicone cup with inner diameter 25 mm and height 10 mm and covered by Mylar foil. Important parameters of such sample preparation procedure (sample consumption, time demanding, etc.) were very

similar to the parameters of procedure previously proposed for LIBS analysis.

2.4. Spectral photometer

Absorption at 1064 nm was measured using spectral photometer with integrating sphere Jasco model V-570. Spectrometer was equipped with tungsten lamp and PbS detector. Samples were poured into 5 mm thick powder cell and BaSO₄ was used as a reference sample.

3. Results and discussion

3.1. Preliminary optimization of LIBS parameters

Optimization of LIBS method is very complicated procedure – there is necessary to find the best combination of at least seven basic equipment parameters (wavelength region, energy of laser pulses, delay between pulses, focal spot diameter, spectrometer slit width, number pulses collected in one analytical point, number of analytical points) providing satisfactory values of basic characteristics of obtained analytical method (LOD, dynamical range, time consumption). Above mentioned LIBS parameters are closely joined together and negligible change of one of them entails necessity of substantial change of the others. Development of LIBS method is thus very time consuming and large amounts of samples are consumed during this process. We decided to perform the optimization of LIBS parameters in two stages (preliminary optimization and selection of best fit calibration) for saving time and reducing sample consumption.

Five samples of V-HMS (four V-HMS-impregnated and one V-HMS-synthesized) were selected for purposes of preliminary LIBS optimization. Concentrations of V in these samples were previously measured by ICP OES after microwave digestion in HF. Distribution of vanadium content in these samples was corresponding to the dynamical range of required final method. Basic parameters of LIBS spectrometer were continuously changed and corresponding spectra were recorded.

First set of spectra was scanned when focal spot diameter was changed from 150 to 400 μm with step 50 μm. Other constant spectrometer parameters were: laser pulse energy 95 mJ, one laser shot per analytical point, 3 analytical points per sample, spectrometer slit width 15 μm. Second group of spectra was scanned with variable number of analytical points per sample – 1, 3, 4, and 9 respectively. Constant parameters in this case were: focal spot diameter 200 μm, laser pulse energy 95 mJ, spectrometer slit width 15 μm and one laser shot per analytical pulse. Next the influence of spectrometer slit width on sensitivity and repeatability of LIBS measurements was tested. This parameter was changed from 15 to 40 μm with step 5 μm, when focal spot diameter 200 μm, laser pulse energy 95 mJ, one laser shot per analytical point and three analytical points per sample were used. Following spectra set was recorded for focal spot diameter 200 μm, laser pulse energy 95 mJ, spectrometer slit width 15 μm and three analytical points per sample, when the number of laser shots per analytical point was changed from 1 to 3. Last variable parameter was laser shot energy. It was changed from 90 to 105 mJ with step 5 mJ, when values of other parameters were: focal spot diameter 200 μm, spectrometer slit width 15 μm, one pulse per analytical point and three analytical points per measured sample. All above mentioned measurements were performed using double pulse mode with inter-pulse delay 7 μs. Scanning of spectra was performed in the analytical window 300 ± 15 nm (Fig. 1) For each set of tested parameters integral net intensities of selected vanadium lines (V₁ – 310.230 nm, V₂ – 311.071 nm and V₃ – 311.838 nm) were obtained by measur-

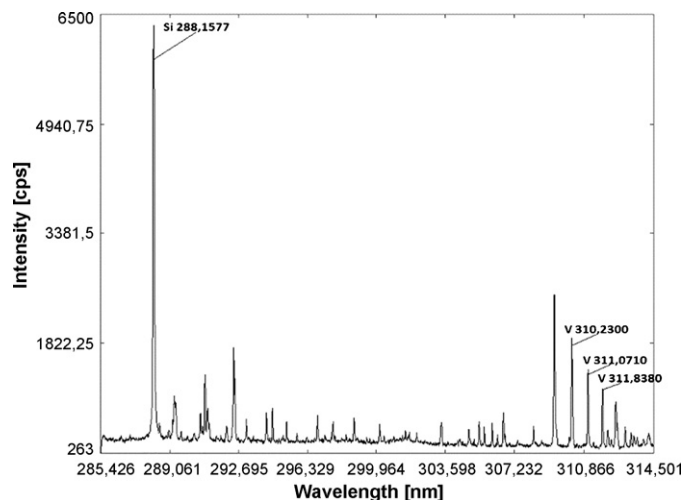


Fig. 1. LIBS spectrum of V-HMS-imp with vanadium concentration 3.5% (w/w) recorded with using next LIBS condition – laser energy 95 mJ, spot diameter 200 μm, spectrometer slit width 15 μm, one laser shot at one analytical point.

ing five V-HMS samples plotted against corresponding vanadium concentrations. Least square method was used for calculation of parameters β_0 and β_1 in next regression equation

$$C_V = \beta_0 + \beta_1 I_V \quad (1)$$

where C_V is the concentration of vanadium in measured V-HMS samples (w/w, %) and I_V is the average net peak area of particular V analytical line (counts s⁻¹). A group of 22 preliminary calibration curves was obtained by such way for each tested analytical line (66 all together) and regression characteristics AIC, MEP and R^2 were used for selection of the best LIBS parameter setting.

One outlier representing only V-HMS-synthesized sample included in the group of measured materials was identified for any of 66 preliminary LIBS calibration curves. Typical situation is depicted in Fig. 2. But no outlier was observed for preliminary ED XRF calibration curve when the same set of five V-HMS samples was used for its construction (Fig. 3).

V-HMS preparation technique obviously influenced some sample feature important for LIBS spectra recording but not significantly important for ED XRF analysis. The adverse effect of

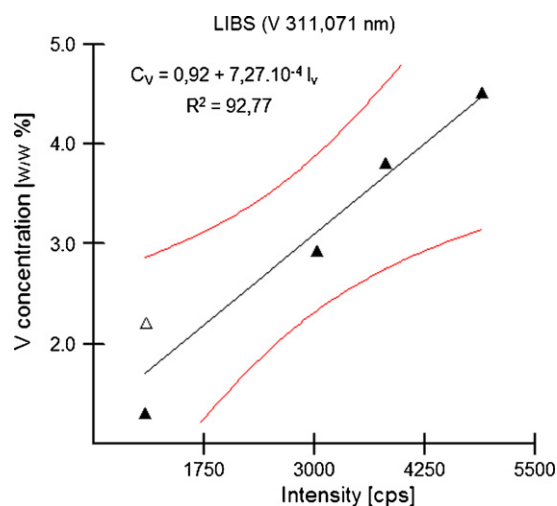


Fig. 2. Preliminary LIBS calibration curve for vanadium line with wavelength 311.071 nm – spectra were recorded with using next LIBS condition – laser energy 95 mJ, spot diameter 200 mm, spectrometer slit width 15 mm, one laser shot at one analytical point.

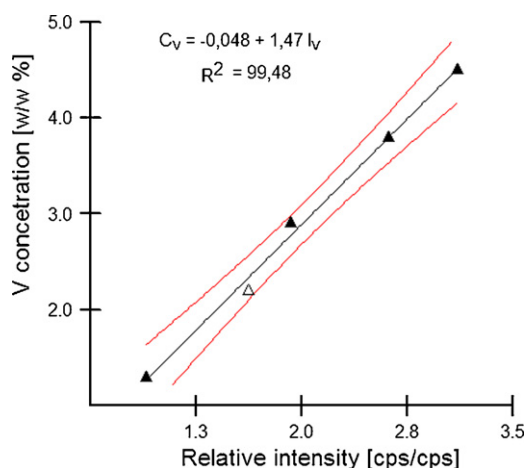


Fig. 3. Preliminary ED XRF calibration curve for vanadium K α line with energy 4.95keV – spectra were recorded with using next ED XRF condition – tube voltage 40 kV, tube current 80 mA, duration of spectra recording 100 s.

differential catalyst preparation procedure on LIBS analysis of vanadium was detectable in wide range of LIBS parameters thus optimization of LIBS setting appeared not to be an effective way for solving the problem. Finally, the decision was made to calibrate LIBS spectrometer using only V-HMS-imp samples. Unfortunately, it was not possible to create the unique method for LIBS measuring of V-HMS-synthesized catalysts through limited number of available V-HMS-synthesized samples.

Optimal conditions for LIBS calibration were selected using preliminary calibration curves after deleting the outlier point belonging to V-HMS-synthesized sample. Regression characteristics AIC, MEP and R^2 of such modified particular preliminary calibration curves were used as fundamental optimization criterions. Set of LIBS parameters demanding curve with minimal AIC and MEP and herewith maximal R^2 was considered to be convenient for subsequent LIBS calibration.

3.2. LIBS calibration

Nine authentic V-HMS-impregnated samples (four previously used for preliminary optimization and five new ones) were used in the process of LIBS calibration. Concentration range of vanadium in employed standards was 1.3–4.5% (w/w). LIBS spectra were scanned under the following conditions: laser energy 95 mJ, spot diameter 200 μ m, spectrometer slit width 15 μ m, one laser shot at three analytical points. Integral net intensities of vanadium analytical line with wavelength 311.071 nm were plotted against corresponding vanadium concentrations and two calibration models were suggested for description of measured data. First one was identical with above mentioned model adopted for preliminary calibration curve (Eq. (1)); second one is described by Eq. (2).

$$C_V = \beta_0 + \frac{\beta_1 I_V}{I_{Si}} \quad (2)$$

when I_{Si} means integral net intensity of silicon line with wavelength 288.158 nm. Calibration curve calculated according to Eq. (1) is depicted in Fig. 4, curve calculated by Eq. (2) in Fig. 5. Significantly worse fitting of curve calculated with using of Eq. (2) shows that the correction on comparison line of Si did not improve the quality of calibration line, thus it was decided not to apply this correction for subsequent measurements.

Limit of detection (LOD) for suggested LIBS method was defined according to the 3σ concept, where σ was the standard deviation calculated from five replicated determinations of vanadium in the real sample with a low concentration of measured element

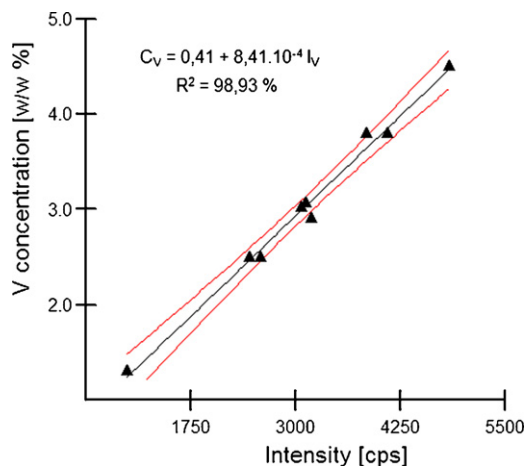


Fig. 4. LIBS calibration curve calculated with using Eq. (1).

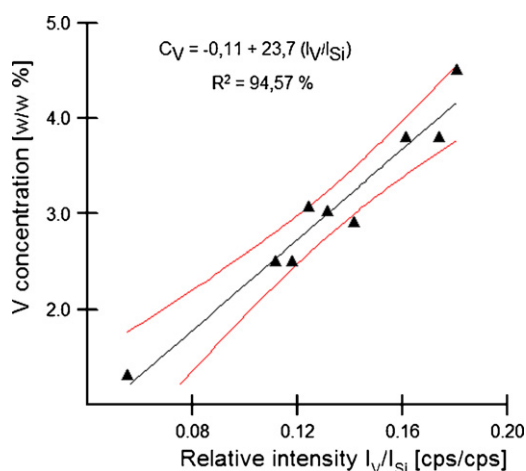


Fig. 5. LIBS calibration curve calculated with using Eq. (2).

(1.5%, w/w). Value of such calculated LOD was 0.13%, w/w. This LOD describes detection ability of suggested methodology, not the real detection ability of used LIBS spectrometer.

3.3. Comparison LIBS and ED XRF

Set of nine calibration V-HMS-impregnated standards previously used for calibration of LIBS was used for calibration of ED XRF spectrometer (Elva X, Elvatech Ltd., Ukraine). Three samples of impregnated and three samples of synthesised V-HMS catalysts were analyzed for vanadium content using both analytical methods. Results of LIBS and ED XRF measurements are summarised in Table 1. If the identical set of V-HMS-imp standards was used for calibration of LIBS and ED XRF, comparable results of V content measurement in V-HMS-imp samples were obtained by both meth-

Table 1
Results of LIBS and ED XRF analysis of real samples of V-HMS catalysts.

Sample	Sample type	LIBS C_V [w/w %]	ED XRF C_V [w/w %]	LIBS/EDXRF [%]
A1	V-HMS-imp	4.43	4.57	96.93
A2	V-HMS-imp	3.02	3.06	98.69
A3	V-HMS-imp	1.99	2.00	99.70
B1	V-HMS-synt	0.35	2.65	13.21
B2	V-HMS-synt	1.35	2.20	61.23
B3	V-HMS-synt	1.48	4.00	37.10

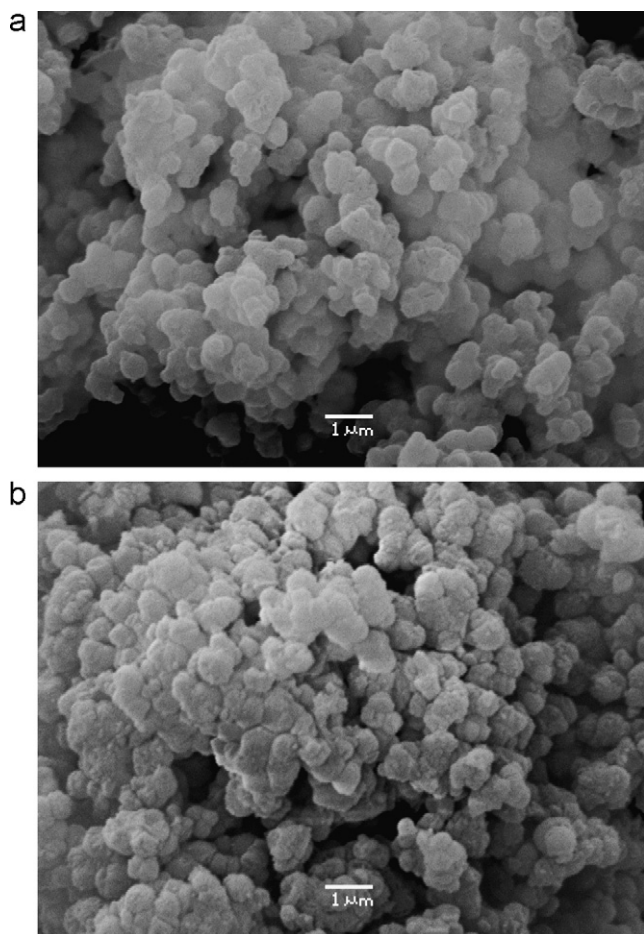


Fig. 6. SEM visualization of V-HMS-impregnated (a) and V-HMS-synthesized (b) samples.

ods. However, results for V-HMS-synthesized samples obtained by LIBS and ED XRF were entirely different.

We postulated three possible sources of different sensitivity of LIBS for synthesised and impregnated samples: (i) difference in particle size distribution, (ii) difference in absorption of excitation beam, (iii) difference in vanadium bonding and distribution.

- (i) Scanning Electron Microscope (SEM) JEOL JSM-5500LV at acceleration voltage of the electron beam 15–20 kV was adopted for visualisation of typical representatives of impregnated and synthesized samples (Fig. 6a and b). The grain analysis was performed using Gwyddion software based on derivation of gray-scale signal for determination of grains' boundary and consecutively diameter of circle with similar area (Fig. 7a and b) Any significant difference in particle size distribution was not observed.
- (ii) Absorption at 1064 nm varied from 0.01 to 0.02 for all V-HMS-imp and V-HMS-synt materials. Thus, any significant difference was not found in the absorption of the wavelength corresponding to the excitation beam.
- (iii) V-HMS-synt and V-HMS-imp materials have a different distribution of isolated monomeric units with tetrahedral coordination, oligomeric units connected by V–O–V bonds and bulk vanadium oxides [1,16]. While monomeric vanadium species were predominantly formed at V-HMS-synt, the octahedrally coordinated vanadium species were more formed at V-HMS-imp. Bulk vanadium species were not formed on V-HMS-synt materials even at high vanadium content (up to

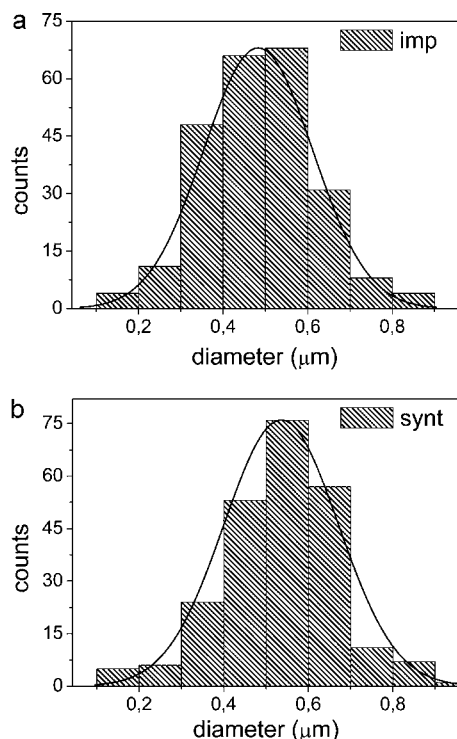


Fig. 7. Particle size distribution of V-HMS-impregnated (a) and V-HMS-synthesized (b) samples.

9 wt.% V), but they were formed at V-HMS-imp materials. Thus, the reason for inability of vanadium content for V-HMS-synt samples when V-HMS-imp standards were used for LIBS spectrometer calibration seems to be a different chemical form of vanadium in both types of materials.

4. Conclusion

The procedure for the analysis of vanadium in samples of V-HMS catalysts using commercially available LIBS spectrometer was developed. Real samples previously analyzed by ICP OES after microwave digestion were used as calibration standards. In the process of LIBS parameters optimisation the strong adverse effect connected with procedure of catalyst preparation was identified. This effect complicates the process of LIBS calibration (different sets of calibration standards have to be used for particular V-HMS sample types) but on the other hand, this effect could be useful for sample type discrimination, if LIBS and ED XRF techniques are employed simultaneously.

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