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The Stability of Sulfide Sorbents Based on Silica in Aqueous Media. Part II. MCM-41 Matrix

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Sulfide sorbents based on MCM-41 have been synthesized. The chemical and thermal stability of the sorbents obtained has been investigated by physicochemical methods. It has been found that the acid treatment of the samples at the boiling point results in insignificant changes in structural, textural and sorption characteristics, demonstrating the total losses of the sorbent up to 15 wt%, which is considered to be connected with the dissolution of the malformed and unstructured particles of a silica matrix. The neutral and alkaline treatment induces more significant changes associated with the starting matrix dissolution (the weight loss is about 25-30 wt%). Nevertheless, the grafted organic functional layer is retained. The sorbents obtained are quite stable in the studied aggressive conditions and able to work over a long period of time in a variety of technological solutions and are not inferior to the well-known commercial sorbents with functional groups.

Keywords: mesoporous mesostructured silica, MCM-41, grafting, stability, treatment, sorption, palladium.

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Стабильность сульфидных сорбентов на основе оксида кремния в водных средах.

Часть 2. Носитель МСМ-41

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Синтезированы сульфидные сорбенты на основе МСМ-41, исследована их химическая и термическая стабильность различными физико-химическими методами. Обнаружено, что кислотная обработка образцов при температуре кипения приводит к незначительным изменениям структурных, текстурных и сорбционных характеристик, демонстрируя общие потери сорбента до 15 масс.%. Указанный факт связан с растворением плохо сформированных и неструктурированных частиц кремниевой матрицы. Нейтральная и щелочная обработка приводит к более значительным изменениям, связанным с растворением исходной матрицы (потеря массы составляет около 25-30 масс.%). Тем не менее привитый органический функциональный слой сохраняется. Полученные сорбенты на основе МСМ-41, как и на основе SBA-15, относительно стабильны в изученных агрессивных условиях и способны работать в течение длительного периода времени в различных технологических растворах.

Ключевые слова: мезопористый мезоструктурированный диоксид кремния, МСМ-41, прививка, сульфидный сорбент, стабильность, обработка, сорбция, палладий.

Introduction

The discovery of mesostructured mesoporous materials in the early 1990s [1] supported the studies in many fields of chemistry [1, 2]. Narrow-pore size distribution, high specific surface area and pore volume make periodic mesoporous silicas promising supports for metal sorbents. Two most common types of periodic silicas include MCM-41, MCM-48 and SBA-15 materials. MCM-41 materials [1] are generally synthesized in a basic medium in the presence of surfactant cations. The pore diameter of the MCM-41 materials usually vary from 20 to 100Å as a function of the alkyl chain length of the surfactant template and synthesis conditions. The solid has periodically ordered structures, which consist of two dimensional hexagonal arrays of uniform mesopores.

In recent years a great number of scientific papers on the stability of mesoporous materials have been published [3-7]. The stability of the MCM-41 silica matrix in various aqueous solutions of acids and alkalines was studied [3, 4, 7]. The limited hydrothermal stability is considered as one of the weaknesses of MCM-41 associated with thermal treatment in water or steam, or both, which was

described by Kim and Ryo [7], where MCM-41 and MCM-48 are reported to disintegrate in water at temperatures above 343 K; the disappearance of the ordered features was ascribed to hydrolysis and collapse of the structure due to the ill-crystallized thin walls. The effect proved to be irreversible, which was observed even at room temperature in wet saturated atmospheres [8, 9].

Cassiers et al. [10] presented a systematic study of various types of relevant ordered mesoporous materials under steam; it was found that MCM-41 is a less stable structure under the applied conditions; 30 vol% H₂O at 400 °C for 48 and 120 h. In [4] the authors published the results concerning the test of SBA-1, SBA-3, SBA-15, MCM-41, MCM48 materials in acidic media (HCl, H₂SO₄, H₃PO₄). They described the mechanism of changes in mesoporous materials occurring according to the following scheme: the micropores were first damaged by the acidic stress, and then the mesopores were partially collapsed or partially blocked. There, the authors found that the material resistance to acidic media is connected with the critical wall thickness and pore diameter threshold.

The authors [11] against observed relatively high stability of the SBA-15 mesoporous lattice during impregnation with aqueous solutions of cobalt nitrate; drying and calcination makes this material a potentially good support for metal and oxide heterogeneous catalysts. We carried out a study [3] where it was shown that the MCM-41 matrix was subjected to insignificant dissolution with the weight loss in the media used. Nevertheless, it retains the highly ordered mesostructured structure. There, the mechanism of the fragmentary material disintegration based on the MCM-41 molecular model and interpretation of the percolation theory were proposed. There are also a great number of publications [12-17] on the methods to increase the hydrothermal stability of these MCM-41 type materials. At present the hydrothermal stability of the silica-based MCM-41 type materials has already a high level comparable to microporous zeolites.

In [18] the peculiarities of the sulfide sorbent synthesis on the MCM-41 and SBA-15 matrices were described. The results showed them to be good metal sorbents. However, to fully understand the capabilities of these materials as sorbents there is no evidence on the technological characteristics of the materials obtained, in particular, concerning their stability. As a result, there originated an idea to study its chemical and thermal stability. The present paper is the second part of the stability study of the sorbents based on novel mesoporous materials. In our recent publication [19] the high chemical and thermal stability of the sulfide sorbent based on SBA-15 under the influence of various aqueous media at the boiling temperature was shown.

Thus, the objectives of the current work are to synthesize a sorbent based on MCM-41 with sulfide functional groups, and to investigate its physicochemical characteristics and stability in aqueous media at the boiling point.

Experimental part

The following reagents were used: tetraethoxysilane (*TEOS*), reagent-grade; rectified alcohol (*EtOH*), cetyltrimethylammonium bromide (*CTABr*): C₁₆H₃₃(CH₃O)₃NBr (Sigma Aldrich, Cat.: 855820); aqueous ammonia, reagent-grade; 3-glycidoxypropyltrimethoxysilane (*GPTMS*): C₉H₂₀O₅Si (Sigma Aldrich, Cat.: 440167); thiophenol (*TPh*): (Sigma Aldrich, Cat.: 89021); anhydrous methanol; sodium metal; toluene, chemically pure; hydrochloric acid, reagent-grade; nitric acid, reagent-grade; and sulfuric acid, reagent-grade.

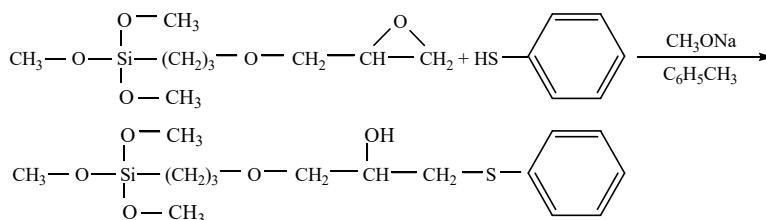
The synthesis of MCM-41 sorbent

The MCM-41 silica was synthesized using the procedure described earlier [20], the reagent molar ratio being:

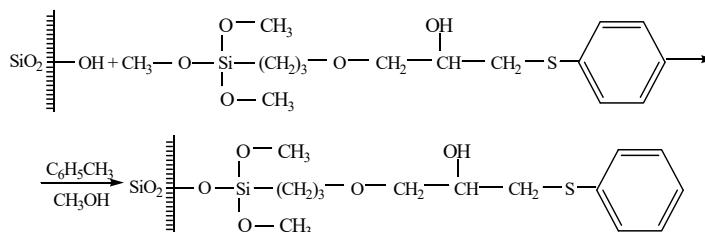


About 3.98 g of CTABr were dissolved in an aqueous-alcoholic solution (400 ml of H₂O and 168 ml of EtOH) at room temperature with intensive mixing. With the dissolving being completed, 89 ml of ammonia solution (pH 12.5) were added. Then, 11.5 g of TEOS were slowly added. The solution was mixed for 2 h. Thereafter, hydrothermal treatment was performed at 120 °C for 2 h. The precipitate obtained was filtered, washed with water and dried in air at room temperature. Calcination in air at 550 °C for 3 h was carried out to remove the organic template from the sample.

The sorbent was synthesized according to the technique described in the patent [21] in two steps. Thiophenol (*TPh*) was attached to the MCM-41 surface over 3-glycidoxypropyltrimethoxysilane (*GPTMS*). 2 g of *TPh* were dissolved in 10 ml of dry methanol, where 0.2 g of metallic sodium were previously dissolved. This mixture was slowly added to a round-bottom flask with two necks, equipped with a thermometer, a reflux condenser and a calcium chloride tube containing 20 ml of dehydrated toluene and 4.3 g of *GPTMS* at 75 °C. The synthesis of 3-(2-hydroxy-3-phenylsulfanylpropoxy)propyltrimethoxysilane (*HPSTMS*) was carried out for 12-14 hours using magnetic stirrer heating at a temperature not higher than 75 °C according to the following reaction:



The chemical modification of the support was performed with HPSTMS according to the following reaction (simple immobilization):



A half amount of HPSTMS was added to 1 g support (MCM-41 $S_{\text{sp.}} \sim 1100 \text{ m}^2/\text{g}$). Then, 10 ml of absolute toluene was added to the resulting suspension. The mixture was heated to 68-70 °C overnight using the magnetic stirrer. The resulting product was separated with the Shott funnel → glass filter using a vacuum pump. The precipitate was carefully washed with toluene and hot ethanol. The resulting sorbent “**M-Sorb**” was dried in air at room temperature.

The sorbent treatment

The experiment included the chemical treatment of the mesoporous silica MCM-41 with the grafted sulfide functional groups. The M-Sorb sample was divided into five parts (samples). These samples were exposed to different aqueous media, such as water, hydrochloric acid, nitric acid, sulfuric acid, and ammonia at the boiling temperature. To treat the samples, 300 mg of the M-Sorb sample were added to the chemical agent into bottom flask. The solid/liquid ratio was equal to 1:100. Then, the suspension was heated to 100 °C and boiled for 1 h. Table 1 shows the detailed conditions for the sample treatment.

After boiling, the sample was filtered and washed with distilled water. Then, the solid residue was dried in vacuum at 80 °C for 6 h. The samples obtained were studied by X-ray diffraction, low-temperature nitrogen adsorption, IR-spectroscopy, thermal analysis, X-ray fluorescence and palladium sorption.

Methods of sample characterization

The X-ray patterns were taken using Cu K α -radiation with the diffractometer X'Pert PRO (PANalytical®, Netherlands) with the PIXcel detector, equipped with a graphite monochromator. The diffraction measurements were registered within the angular range 2Θ 0.40-7.04°, the step being 0.026° and accumulation time – 120 s at each point.

The nitrogen adsorption-desorption isotherms were obtained using the volumetric adsorption system ASAP 2420 (Micromeritics®, USA) at T=77 K in the range of differential pressures (P/P_0) 0.06-0.99 with the step being 0.015. The specific surface area was calculated using the BET model [22] in the range of (p/p_0) 0.06-0.25, and pore distribution according to the size – using the BJH and KJS isotherm equation [23, 24].

The IR-spectra were recorded using the IR-spectrometer “Tensor 27” (Bruker®, Germany) (at the Center of Collective Use of KSC SB RAS) within the range of 500-4000 cm⁻¹ using the standard technique of sample tableting with KBr (weight ratio of sample/KBr = 1:1000). The sample/KBr ratio was equal to 1:400. The sample weight was 1 mg.

The thermal analysis (TA) of the samples was made in platinum crucibles using the thermal analyzer SDT Q600 (TA Instruments®, USA). Before the analysis the samples were kept in a desiccator at a temperature of 23 °C and air humidity of 30 %. The sample weight was equal to 5 mg, the scanning range being 40-900 °C, with the heating rate of 20 °C/min.

Table 1. The conditions of sample treatment. The treatment time – 1 h, the treatment temperature – 100 °C

№	Sample	Chemical agent	Weight loss(%)
1	M-HCl	1M HCl	14
2	M-HNO ₃	1MHNO ₃	14
3	M-H ₂ SO ₄	1M H ₂ SO ₄	14
4	M-H ₂ O	H ₂ O	24
5	M-NH ₃ aq	0.1 MNH ₃ aq	34

The sulfur and palladium content was determined by X-ray fluorescence (XRF), using a spectrometer "Axios Advanced" (PANalytical®, Netherlands). The spectra within the wavelength range of the periodic table were recorded, and the semi-quantitative analysis of the element content was performed using the program IQ⁺.

The palladium (II) sorption was carried out from the chloride solution under static conditions. 50 mg of the sorbent were placed into a 50 ml conic flask with a rubber plug. 10 ml of the solution containing palladium 11 mmol/l in 0.1M HCl in the flask were added. The contact time between the solution and the sorbent sample was 24 hours with the constant stirring using a laboratory shaker at a stirring rate of 170 rpm. After the separation (using "a blue ribbon" filter) the solid residue was washed with distilled water and dried in air at room temperature. Then, the palladium and sulfur contents of the dry sorbent were determined by X-ray fluorescence.

Results and discussion

The current investigation is directed to the study of three physicochemical characteristics, namely, the pore structure, the grafted layer and the sorption ability. Also, in the course of the experiments the sample weight was controlled. Table 1 shows that the sorbent treatment under rigid conditions results in the weight loss of the samples. The weight loss is especially significant in the case of using more alkaline media: water and ammonia. After the acidic treatment the sample weight loss was 14 %, and after the treatment with water and ammonia it amounted to 24 and 34 wt%, correspondingly. The weight loss after the treatment is likely to be associated with the partial dissolution of the silica matrix, partial washing-out of the grafted functional layer, and the sample loss during the treatment procedure (decantation, filtration etc.).

The X-ray results are not given here because the X-ray patterns do not reveal the porous structure of the material as a consequence of the full pore-filling after grafting. The isotherms of low-temperature nitrogen adsorption and pore size distribution are presented in Fig. 1. The MCM-41 matrix is characterized by the IV-type isotherm according to the IUPAC classification, but after grafting the isotherm is becoming a nearly straight line, indicating the surface absence. The acidic treatment hardly changes the form of the isotherm, while the treatment with water and ammonia results in more significant consequences.

The pore size distribution is shown for the adsorptive area of the isotherm, that gives a more reliable distribution in the presence of hysteresis (Fig. 1b). A more detailed consideration of the nitrogen adsorption data shows that after grafting (the M-Sorb sample) the surface area dramatically falls from 1023 to 9 m²/g as well as the pore volume – from 1.11 to 0.04 cm³/g. In this case, the pore diameter is too small to be determined. As is shown in Table 2 the acidic treatment expands the pore diameter up to 25 Å. The treatment with water and ammonia expands the pore diameter only up to 19 Å and influences the silica matrix rather than the grafted organic matter. The treatment using ammonia, as is shown in Fig. 1, affects the silica framework and shifts the pore volume maximum till disappearance. The liberation of the sample surface treated in the acidic media is likely to occur due to the dissolution of small malformed silica particles in the pores. Their dissolution explains the weight loss of the samples, and increase in the specific surface and pore volume (Table 1 and 2).

The functional groups contained in the samples were identified using IR-spectroscopy. The results showed that after grafting the changes take place in three main wavenumber ranges. 2930-

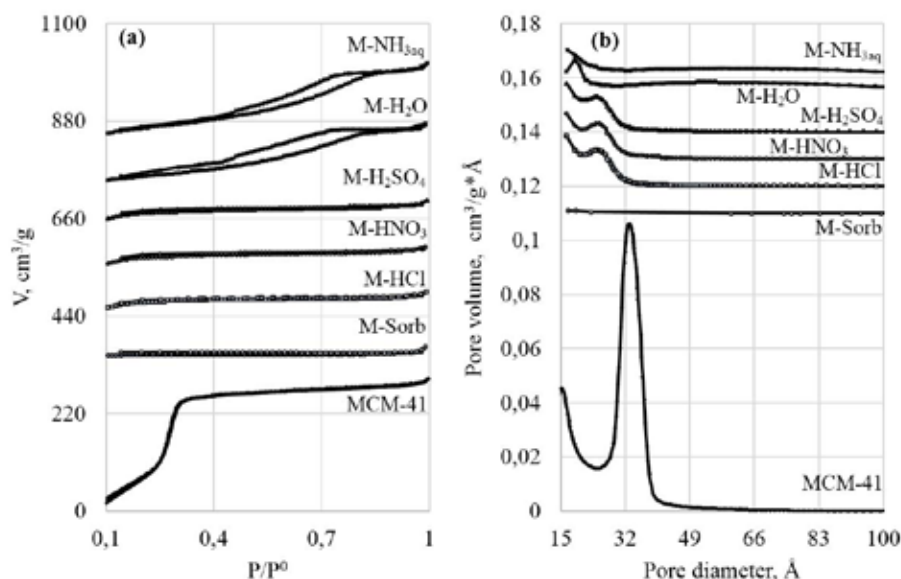


Fig. 1. The nitrogen low-temperature adsorption isotherms (a) and the pore size distribution plots (b) for the samples of original MCM-41 and sorbent (M-Sorb) before and after treatment in different aqueous media. The isotherms are shifted along Y-axis from each other for $\sim 100 \text{ cm}^3/\text{g}$ and pore size distribution plots – for $\sim 0,25$ units

Table 2. The textural characteristics of MCM-41 sorbent samples

№	Sample	$S_{\text{BET}}(\text{m}^2/\text{g})^{\text{a}}$	$V_{\text{BJH}}(\text{cm}^3/\text{g})^{\text{b}}$	$D(\text{Å})^{\text{c}}$
1	MCM-41	1023	1.11	33
2	M-Sorb	9	0.04	– ^d
3	M-HCl	281	0.22	25
4	M-HNO₃	283	0.22	25
5	M-H₂SO₄	287	0.23	25
6	M-H₂O	202	0.34	19
7	M-NH_{3aq}	237	0.40	– ^d

^aBET surface area;

^bBJH adsorption pore volume;

^cPore size is the pore diameter at which pore volume has maximum value in BJH adsorption dV/dD curve;

^dPore volume has no maximum value in BJH adsorption dV/dD curve.

2960 cm^{-1} corresponds to $\nu(\text{C-H})$ stretching vibrations; $1400\text{-}1600 \text{ cm}^{-1}$ being $\nu(\text{C-C})$ ring stretching vibrations; and $570\text{-}710 \text{ cm}^{-1}$ being weak $\nu(\text{C-S})$ stretching vibrations (Fig. 2). The above indicated absorption bands in the spectra after grafting evidence the modifier integration into the pore structure of the MCM-41 matrix and correspond to the thiophenol groups. The treatment of samples under the conditions used do not affect on the graft layer of the sulfide sorbent.

The functional grafting content was determined by thermal analysis (TA). The curves of the weight loss for the samples obtained are given in Fig. 3. Two main processes are presented on the thermogram: the loss of the adsorbed water and organic component. Since the removal of the oxidation products from the pores is associated with diffusive difficulties, the decomposition

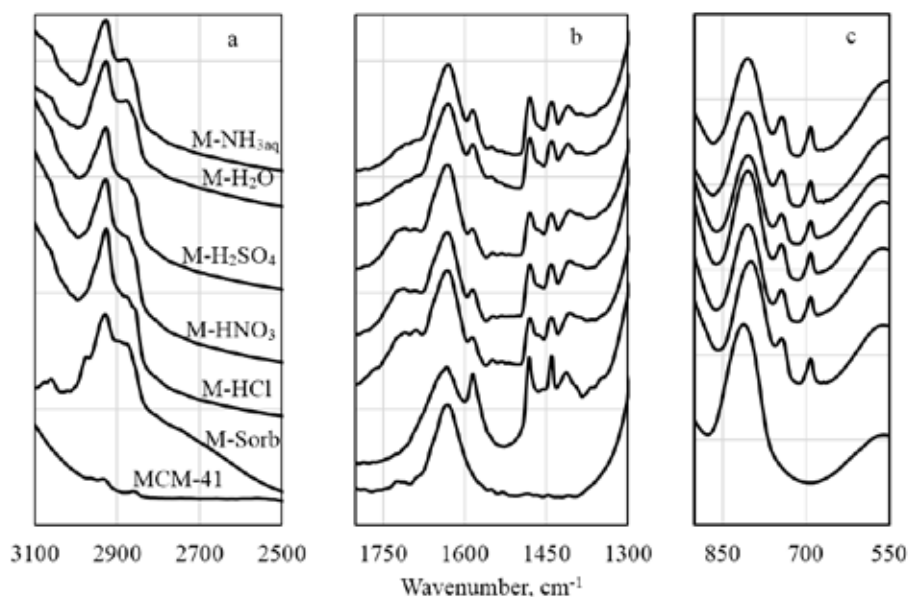


Fig. 2. Infrared spectra of MCM-41 sorbent samples after treatment: a – area 2500-3100 cm^{-1} , b – area 1300-1800 cm^{-1} , c – area 550-900 cm^{-1} .

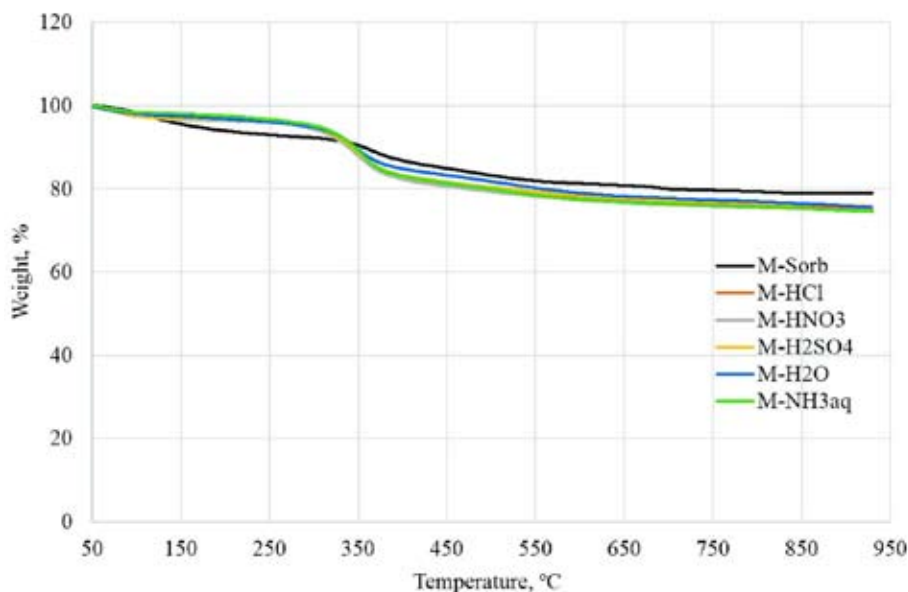


Fig. 3. Thermogram of the MCM-41 sorbent samples

is time-expanded. After the sample treatment the sample behaviour is almost identical, but the organic content is increased according to the TA data (Table 3). The increasing organic content is apparently connected with the decrease of the silica part in the samples after the treatment, which is confirmed by the XRF data. The sulfur content in the initial sorbent (the M-Sorb sample) is 0.86 mmol per gram, but after the treatment it increases up to 1.16 mmol/g in the case of the

Table 3. The influencing a various treatment on grafted group content and sorption capacity for MCM-41 sorbent samples

Sample	Organic content by TA, wt%	S content, mmol/g	Pd content, mmol/g	S/Pd ratio	Pd/Cl ratio
M-Sorb	14	0.86± 0.05	0.63± 0.02	1.4	1.7
M-HCl	22	0.93± 0.05	0.43± 0.02	2.1	1.1
M-HNO₃	22	0.94± 0.05	0.54± 0.02	1.8	1.7
M-H₂SO₄	21	0.99± 0.05	0.61± 0.02	1.6	1.5
M-H₂O	21	1.15± 0.05	0.63± 0.02	1.8	1.2
M-NH₃aq	24	1.16± 0.05	0.66± 0.02	1.8	1.2

treatment with ammonia (about 26 %). This would imply that the insignificant loss of silica after the treatment results in the sharp increase of the organic content in the sample. This fact is associated with the great difference of the molecular weight between the silica unit and the modifier molecule: about 60 gram per mol versus about 350 gram per mol, correspondingly. The sorbent treatment is accompanied by the dissolution of malformed and/or unstructured particles of the silica matrix, which is the cause of the weight loss (Table 1) and increasing organic content (Table 3) after the sorbent treatment. However, the treatment does not result in significant changes in textural and sorption characteristics, while the functional grafted layer is retained. Also, the authors [25] do not recommend using ammonia medium for the real applications of such mesoporous silica materials due their amorphous framework.

The palladium(II) sorption on the studied samples was carried out from the chloride solution. The initial palladium concentration in solution was about 0.011 mol per liter. According XRF data after the sorption the S/Pd ratio is about 1.5-2, while the Pd/Cl ratio is about 1-1.5 as shown in Table 3. At the average, the value of total sorption capacity of sulfide sorbent is 0.6 mmol per gram.

Conclusion

The sulfide sorbent based on the mesostructured mesoporous silica MCM-41 was synthesized using the grafting method. The influence of aqueous media at the boiling temperature on the stability of the sorbents based on the MCM-41 matrix functionalized with the 3-(2-hydroxy-3-phenylsulfanylpropoxy) propyltrimethoxysilane was studied for the first time. The initial samples (the matrix and its sorbent) and the treated samples were characterized by the X-ray diffraction, low-temperature nitrogen adsorption, IR-spectroscopy, thermal analysis and palladium(II) sorption. The organic content and sorption ability were controlled using X-ray fluorescence. It was found that the acidic treatment was accompanied by the dissolution of the compact malformed and/or unstructured particles of the silica matrix, demonstrating the total loss of the sorbent up to 15 wt%. The treatment with water and ammonia induces more significant changes in the matrix associated with the starting matrix dissolution (the weight loss is about 25-30 wt%). Nevertheless, the grafted functional layer is retained. The sorbents obtained are quite stable in the studied aggressive media and are able to function over a long period of time in a variety of technological solutions and are not inferior to the well-known commercial sorbents with functional groups.

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