

Impact of Supercritical Drying with Excess Solvent on Textural Properties of Ti-HMS Catalyst Support

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Textural characteristics of catalysts and catalysts supports are of a prime importance when it comes to their application in processing of high molecular weight compounds. Drying procedure is a key factor in preservation of wet gel properties. Hexagonal mesoporous silicas (HMS) doped with Ti-ions is finding a promising usage as heterogeneous catalysts support. In this paper, the effect of supercritical drying with excess solvent on the textural characteristics of Ti-HMS is addressed. HMS with Ti ions (Si/Ti atomic ratio of 40) is prepared using the sol-gel method. Dodecylamine is used as the structure directing surfactant (*S*) and TEOS and Titanium butoxide as the inorganic precursors (*I*). Specific surface area, mesoporosity and pore volume of the support dried by thermal evaporation of solvent in air and dried in excess of supercritical ethanol are compared. The results indicate that improved specific surface area and almost four times bigger value for mesopore volume are obtained using supercritical drying procedure.

Key words: catalysts, mesoporous catalysts, sol-gel method, drying method, petroleum fractions.

Introduction

In recent years, porous materials have found their application as heterogeneous catalysts and catalysts supports for numerous petroleum processes [1, 2]. The most widely used are zeolites, microporous crystals with a narrow pore size distribution and average pore diameter less than 2 nm. However, small pores sizes become an important obstacle when large, bulky molecules need to be processed. Their diffusion inside the pores is limited and therefore active sights within the pores become unavailable. In the last decades, much research is focused on catalysts pore size enlargement from micropore to mesopore range, while retaining narrow size distribution. Accordingly, new family of ordered mesoporous materials aroused. It is believed that they will improve some commercial processes in the future, by superseding zeolites and amorphous silica-alumina catalysts [2].

The first ordered mesoporous material was synthesized by the scientists from the Mobil Oil Research and Development. Moreover, they were the first to explain and recognize extraordinary properties of this material [3]. Using cationic surfactants as a template to assemble silicate anions from solution, three members of the Mobil Composition of Matter (denoted as MCM) were reported: MCM-41 with hexagonal array of uniform pores, MCM-48 with cubic and MCM-50 with lamellar mesostructure [4]. This discovery was a breakthrough in engineering of materials and accelerated progress of new mesoporous silicas [5]. In order to improve the template removal from the pores and lessen pore blockage, Zhang et al. [6] and Pauly et al. [7] have developed additional approach for the preparation of the mesoporous silica. It was based on neutral templating mechanism. They have used primary amines as a neutral surfactant to synthesize

HMS (hexagonal mesoporous silica). In this case, H-bonding was the driving force for the structure formation and therefore surfactant extraction is easier and almost complete. Tanev et al. [8] have compared physical properties of MCM-41 and HMS and found similarities in high values of surface areas (around 700-1000 m²/g) and pore volumes. These are important advantages for using these materials in catalysis, since a high surface area allows high concentrations of active sights. Another advantage that HMS silica possesses is a thick framework wall which contributes to superior thermal stability required for the catalytic applications.

Some research in the application of MCM-41 and HMS in hydrotreating reactions has been done recently. Corma et al. [9, 10] tested NiMo/MCM-41 for hydrodesulphurization, hydrodenitrogenation and hydrocracking reactions and reported better activity in comparison with other supports- amorphous silica-alumina and USY zeolite. Montesinos-Castellanos et al. [11] modified HMS with the incorporation of heteroatoms within their framework and reported that the presence of Al, Ti and Zr ions increased the hydrogenation ability of NiMo catalysts in the reaction of naphthalene. Similar conclusion made Halachev et al. [12] for NiW/(P)Ti-HMS catalyst. Zepeda et al. [13, 14] stated increased pore diameter with Ti incorporation, as a result of a higher bond length of Si-O-Ti than Si-O-Si length. Numerous studies made with the conventional active metals CoMo, NiMo, CoW, NiW supported on Al-, Ti-HMS [13-16] claim enhanced HDT activity with these supports.

The crucial advantage for catalytic application of these materials is heteroatoms incorporation, and development of the appropriate surface acid sights [17]. Homogeneity at the molecular scale influences the acidic properties [18-20].

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Therefore, the choice of the preparation method is important. Conventional syntheses procedures, like precipitation and coprecipitation methods, are very limited in fine controlling of component mixing because of the differences in the pHs and rates of hydroxides precipitation [21, 22]. On the other hand, the sol-gel process allows homogeneous formation of heterolinkages even at low temperatures [17, 23, 24]. Toba et al. [25, 26] examined titania-silica and titania-alumina xerogels made by coprecipitation and sol-gel method and found higher acidity in the sol-gel samples attributed to a higher density of hetero-linkages formed. Also, the surface area found in titania-alumina sample was considerably larger in sol-gel sample.

In view of the fact that HMS silica is synthesized using sol-gel procedure and solvent needs to be removed prior to calcination, the applied drying procedure is the key factor in determining the textural characteristics. The most frequently used drying procedure - thermal evaporative drying in air causes the formation of capillary pressures at the liquid-vapor interface, reaching values of up to 100-200 MPa [27] and therefore could cause structural collapse and reduction of mesoporosity [28, 29]. Obtained xerogels contain significant fraction of micropores and reduced surface areas. In order to overcome that problem, some researchers have tried to age the gel in the silane precursor, alcohol or water bath and in that way increase the network stiffness prior to drying [30-32]. In contrast, an aerogel is a gel from which the liquid has been removed in such a way as to prevent significant collapse or change in the structure as liquid is removed. This is typically accomplished by heating the liquid-filled gel in an autoclave while maintaining the prevailing pressure above the vapor pressure of the liquid until the critical temperature of the liquid has been exceeded, and then gradually releasing the vapor, usually by gradually reducing the pressure either incrementally or continuously, while maintaining the temperature above the critical temperature. The critical temperature is the temperature above which it is impossible to liquefy a gas, regardless of how much pressure is applied. At temperatures above the critical temperature, the distinction between liquid and gas phases disappears and so do the physical manifestations of the gas/liquid interface. In the absence of an interface between liquid and gas phases, there is no surface tension and hence no surface tension forces to collapse the gel. Such a process is called "supercritical drying in excess solvent." Aerogels produced by supercritical drying typically have high porosities (50-99 vol%), lower microporosity, higher surface areas and gives amorphous mixed oxide aerogels [33-41]. Calvino et al. [42] examined the influence of the way of drying on textural characteristics of 10% titania - 90% silica and found the following order for the surface areas: 459 m²/g for xerogel, 515 m²/g for alcogel (supercritical drying with CO₂ at 315K) and 832 m²/g for aerogel (supercritical drying in alcohol at 600K). Brodsky et al. [43, 44] reported higher average pore diameter observed in titania-silica aerogels and alcogels with the higher supercritical drying temperature.

The objective of this work is to investigate the influence of supercritical drying with excess solvent procedure on textural characteristics of Ti-HMS supports. Two Ti-HMS supports were synthesized. One was dried by a thermal evaporation in air, and the other was dried in excess of SC ethanol.

Experimental part

Materials

Ti-substituted mesoporous silicas were synthesized using

tetraethyl ortosilicate (TEOS, Aldrich 98%) and titanium butoxide (Ti-but, Aldrich 97%) as inorganic precursors. Surface directing agent was dodecylamine (C₁₂H₂₅NH₂, DDA, Aldrich 98%).

Preparation of the catalyst supports

In order to examine the influence of the drying process on textural characteristics, two different Ti-HMS supports were synthesized. The procedure for the synthesis of pure hexagonal mesoporous silica (HMS) was first proposed by Tanev and Pinnavaia [7, 8]. It was based on the neutral S[°]I[°] templating route and H-bonding between neutral inorganic precursor (I[°]) and neutral primary amine (S[°]) as a surface directing agent. The incorporation of the Ti heteroatom was done following the procedure published by Gontier and Tuel [45]. The molar composition of the reaction mixture was: 0.1TEOS:0.025Ti-but: 0.65EtOH:0. 1isopropyl alcohol: 0.027DDA: 3.6H₂O: 0.002HCl. Basically, the first solution (A) was obtained by mixing TEOS, Ti-but, EtOH and isopropyl alcohol. The second solution (B) was dissolved DDA in water and HCl. Solution A was slowly added to solution B while vigorously stirred and the stirring was maintained for half an hour. The reaction products were aged at ambient temperature for 1.5 hours, filtered under vacuum and washed several times with ethanol (with total ethanol amount of 100 ml). Two catalyst supports were obtained using this mixture in the following way: one support, aerogel, was dry in excess of supercritical ethanol on 100 bars and 528 K for half an hour and another, xerogel, was dried at room temperature for 24 hours. Subsequently, both samples were calcined in air at 823 K for 4 h, with heating rate of 2.5 K/min, being held for a half an hour on 823 K.

Supercritical drying in excess of solvent

Catalyst support, prepared by previously described procedure, was transferred to the pressure vessel (Autoclave Engineers BTRS-Jr, Division of Snap-title, Inc., Erie, PA, USA) and the vessel was filled with additional 170 ml of ethanol. Such a procedure was necessary to ensure that the pores in the obtained material were always filled with single phase ethanol (liquid, supercritical or gas) thereby avoiding formation of the two phase region (liquid-gas) in the pores [46, 47, 48]. The vessel was then sealed and heated (heating rate 3.3 C°/min, total time of heating was 70 min) to the desired temperature and pressure of 100 bars and 528 K. Upon the reaction completion, after half an hour, the system was depressurized to atmospheric pressure followed by gradual temperature decrease to ambient conditions.

Characterization of the samples

Textural parameters were estimated using N₂ adsorption-desorption isotherms recorded at 77 K on Thermo Finnigan Sorptomatic 1990. The samples were degassed in vacuum prior to the analysis, at 373 K for 2h and subsequently at 473 K for 16 h. Specific surface area was calculated by applying BET equation to the range of relative pressures from 0.05 to 0.16. The t-plot analysis was another method used to evaluate textural properties of the samples. This method is frequently used for the characterization of porous materials. The average pore diameter and mesopore volume were calculated using the Barret-Joyner-Halenda method (BJH) to the desorption branch of isotherm and the Dollimore and Heal model to the adsorption branch. The cumulative pore volume was obtained using the Gurvich model. The assessments of microporosity were made using the Dubinin and Raduskevich correlation.

The Ti-ion incorporation in all four supports was conformed on FT-IR spectrophotometer, Thermo, Nicolet iS10, with ATR, operating in wavelength range from 4000 cm⁻¹ to 600 cm⁻¹.

The substrate and catalysts morphology and Ti concentration was determined by Scanning Electron Microscope (SEM) JEOL JSM-6610 LV, equipped with an Energy Dispersive X-ray Spectrometer (EDS) Oxford X-Max. To reduce charging effect, the samples were coated with a thin (5nm) conducting layer of gold. An electron microprobe used in an energy dispersive mode (EDX) was employed to obtain information on the titanium dispersion in the samples.

Results and discussion

FT-IR spectroscopy of calcined supports

Ti-O-Si bonds formation was determined by IR spectroscopy. The IR spectra of four catalyst supports are shown in Fig.1.

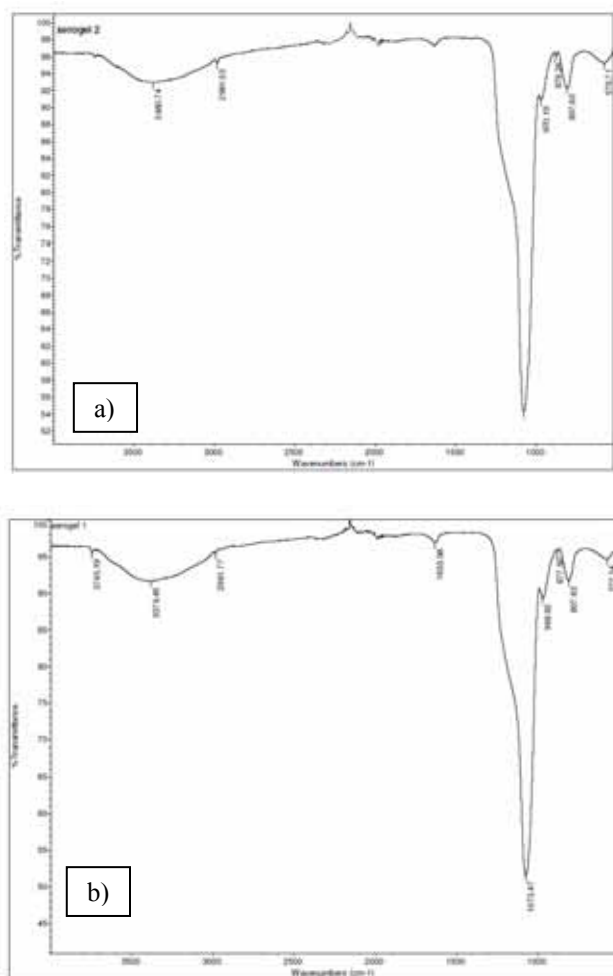


Figure 1. FT-IR images of Ti-HMS supports: a) dried by thermal evaporation in air, b) dried with SC solvent excess.

The asymmetric vibration of Si-O-Si bond shows band at 1087 cm⁻¹ and its shift to lower wavenumbers is observed when Ti-ions are incorporated into the HMS structure [49]. This band is positioned at ca. 1073 cm⁻¹ for all four measured supports. Moreover, the literature reports that the IR band appearing in the region from 910 to 970 cm⁻¹ is a characteristic vibration caused by the formation of Ti-O-Si bonds [50, 51]. Its exact position depends on chemical composition of the sample and the instrument characteristics. According to that, the band at ca. 970 cm⁻¹ found in all four samples can be assigned to the stretching vibration of $\nu_{as}(\text{Si-O-Ti})$ group. However, this is not a definite proof, since Ti-free silicates also exhibit similar band. Therefore, it is necessary to compare its intensity to the intensity of the band at ca. 802 cm⁻¹, indication of symmetric stretching vibration of $\nu_s(\text{Si-O-Si})$ [52]. When the intensity of

the band at ca. 970 cm⁻¹ is enhanced compared to the intensity of the band at ca. 802 cm⁻¹, then this can be taken as an indication of Ti-ions incorporation [53]. This enhancement can be seen in Fig.1. The more enhanced it is, the more Ti-O-Si linkages are formed.

Furthermore, hydrogen bonding between silanol groups is displayed by the broad band at ca. 3380 cm⁻¹. This band, found in the hydroxyl region, is an indication of $\nu_{OH}(\text{Si-O-H})$ vibration. In the pure silicates, it is usually found at higher wavelength, ca. 3445 cm⁻¹. This shift reveals more hydrogen bonding with Ti incorporation caused by the existence of defective sites.

N₂ adsorption-desorption isotherms

The physical adsorption-desorption isotherms of nitrogen was used to determine the textural properties of the supports and recorded isotherms are shown in Fig.2.

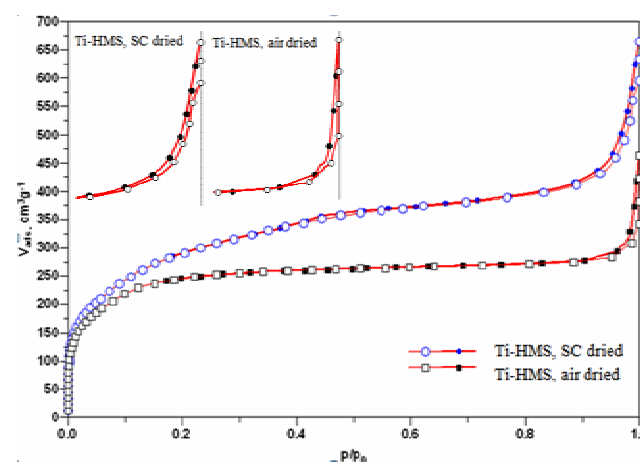


Figure 2. Comparison of N₂ adsorption-desorption isotherms of Ti-HMS support dried in excess of supercritical ethanol and the support dried by thermal evaporation in air

From Fig.2 it can be seen that the isotherms of the supercritically dried material resemble more IUPAC type IV isotherms [54], expected for mesoporous silicas. It is also seen that the aforementioned support has adsorbed much more nitrogen than support dried by thermal evaporation for the same relative pressures. That is the indication of a higher specific surface area and bigger total pore volume obtained, as it is evidenced by the results given in Table 1. Moreover, the sharp nitrogen uptake at low relative pressures, found for both samples, indicate a well developed micropore region, which also added to valued to high surface area obtained. Another increase in the relative pressures range of $p/p_0=0.2$ to 0.5, more pronounced for SC dried support, results from better developed mesopores region and therefore capillary condensation of nitrogen inside the pores occur [55]. Shift of framework confined mesopores filling to higher relative pressures found with this support indicates an increase in framework pore size, as well. Moreover, at high relative pressures, bigger than 0.9, both samples had significant uptake of N₂, characteristic for the materials containing mesopores at the upper limit of mesoporosity [53]. Both hysteresis loops close at relative pressures above 0.85, have narrow shape with almost parallel adsorption and desorption branches, confirming the existence of larger mesopores.

In order to make a quantitative comparison of drying procedure influence on the textural parameters, calculated values, such as specific surface area derived from both BET equation and t-plot analysis, S_p , cumulative pore volume obtained using the Gurvich model, V_p , volume of the mesopores calculated using BJH and Dollimore and Heal correlation, $V_{p, \text{meso}}$ and average pore diameters $D_{p, \text{avg}}$ of the

supports are given in Table 1.

Table 1. Textural parameters of Ti-HMS supports.

Sample	Ti-HMS, thermally evaporated in air	Ti-HMS, SC dried
S_{BET} , m ² /g	868	1100
$S_{t\text{-plot}}$, m ² /g	851	1015
aV_p , cm ³ /g	0.471	0.790
$^bV_{p,meso,(BJH)}$ cm ³ /g	0.116	0.495
$^cV_{p,meso,(DH)}$ cm ³ /g	0.143	0.422
$^bD_{p,avg,(BJH)}$ nm	3.93	4.33
$^cD_{p,avg,(DH)}$ nm	3.66	6.34

^a Calculated by Gurvich model, at $p/p_0=0.98$.

^b Calculated by BJH model.

^c Calculated by Dollimore and Heal model.

BET surface areas found for both supports have high values, bigger than 850 m²/g. Very similar values for total surface areas resulted from the t-plot analyses with t-parameter in the range of 0.13 to 0.25 nm. These results show that the surface area is improved by a factor of 1.26 and total pore volume by a factor of 1.6 with supercritical drying. Mesopore volumes found for thermally evaporated support are 0.116 cm³/g and 0.143 cm³/g, depending on the model used for calculation. Values for SC dried sample are 0.495 cm³/g and 0.422 cm³/g. Mesopore volume in thermally evaporated sample accounts for 25% of total pore volume while in SC sample it is enhanced to 63%. Almost four times bigger value for mesopore volume is obtained with SC dried sample. Such a strong improvement is a result of preserved wet gel structure while SC drying. Actually, as the esterification reactions take place during high temperature SC drying with ethanol, the surface Si-OH group are modified into hydrophobic Si-OR groups. Moreover, the excess of ethanol prevents solvent evaporation inside the pores during initial heating in the autoclave, and shrinkage of gel before SC conditions are reached. Consequently, specific surface area and pore volume increase.

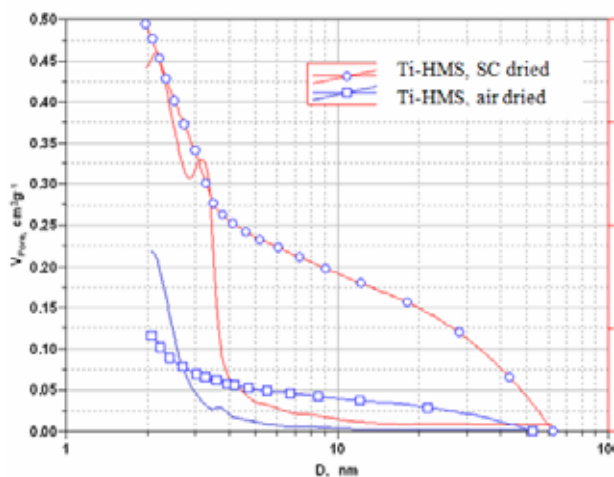
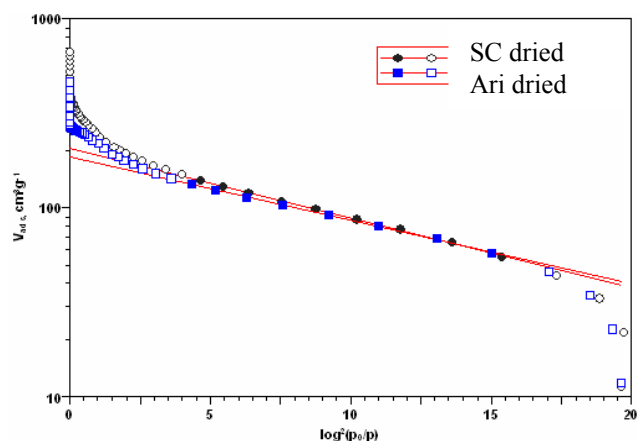


Figure 3. Comparison of cumulative pore volume in the mesopore region of Ti-HMS support dried in excess of supercritical ethanol and the support dried by thermal evaporation in air.

Graphical comparison of mesopore region of both samples is given in Fig.3. Better preserved mesoporosity with CS drying is clearly visible. Furthermore, mean pore diameter is enhanced from 3.93 to 4.33nm. Both these values are higher than previously reported results of Gontier et al. [45] for pure silica materials. This is expected since titanium cations have radius larger than Si⁴⁺ cations, so the length of Si-O-Ti bond is bigger than Si-O-Si bond.



Figures 4. Dubinin and Raduskevich graphs used for micropore volume calculation of two supports.

The textural parameters of micropore region are analyzed using correlation of Dubinin and Raduskevich. The obtained graphs are given in Fig.4, and calculated results are presented in Table 2.

Table 2: Micropore volume and fraction of two supports calculated using Dubinin and Raduskevich correlation.

Sample	Ti-HMS, thermally evaporated in air	Ti-HMS, SC dried
$V_{p,micro}$, cm ³ /g	0.287	0.320
Micropore fraction, %	60	40

The results from Table 2 reveal a reduction in micropores volume fraction in total pore volume from 60% to 40% using SC drying procedure. This confirms that the pressures evolved in mesopores during phase transformation from liquid to gas state while thermal evaporation of the solvent caused the gel-network shrinkage and mesopores volume reduction in favor of micropores.

SEM-EDS analyses of catalyst supports

SEM-EDS analyses were used to examine the morphology of the particles and the homogeneity of the Ti distribution in the HMS framework.

In Fig.5 the SEM images of the studied samples are presented. These micrographs show that Ti-HMS is comprised of sphere-shaped particles, smaller than 1μm in diameter. This is in accordance with the previous findings of other authors [55]. These particles are organized in nonuniform agglomerates. Comparing the particle sizes of the prepared supports indicates that the particles of support dried using excess of SC solvent are smaller in diameter, providing material with much finer morphology. This correlates to a higher specific surface area value obtained from the adsorption measurements. Also, this should influence the increase of textural mesoporosity, which does not arise from the framework pore volume, but from the interparticle voids.

Appropriate titanium dispersion is important for generation of acid sights in the support. Sol-gel method provides superior mixing at the molecular level and homogeneous formation of heterolinkages. Moreover, the average bond angle of Ti-O-Ti is 159° and of Si-O-Si is 152°; the average bond lengths are 1.8Å for Ti-O and 1.6Å for Si-O. These similar structural properties and low Ti content in the samples allow homogeneous substitution of Si for Ti in the silica matrix. However, some reports from the literature suggest that the wet gel structure and intimate mixing would not be preserved during supercritical drying with alcohol, so called high temperature drying, because the segregation of anatase occurs [56]. On the contrary, SEM-EDS of our samples, shown in

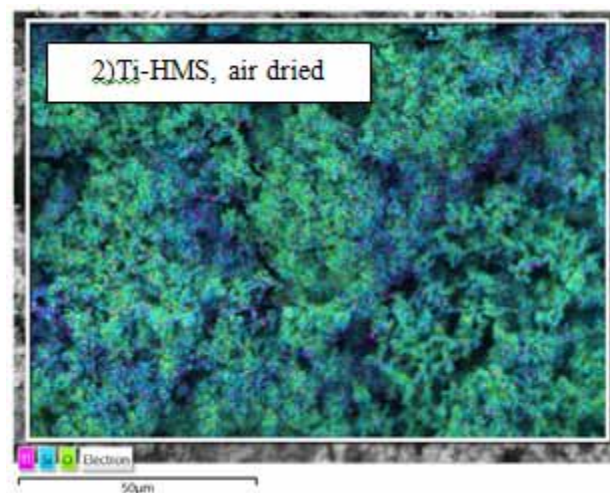


Figure 6. SEM-EDS images of Ti dispersion in supports

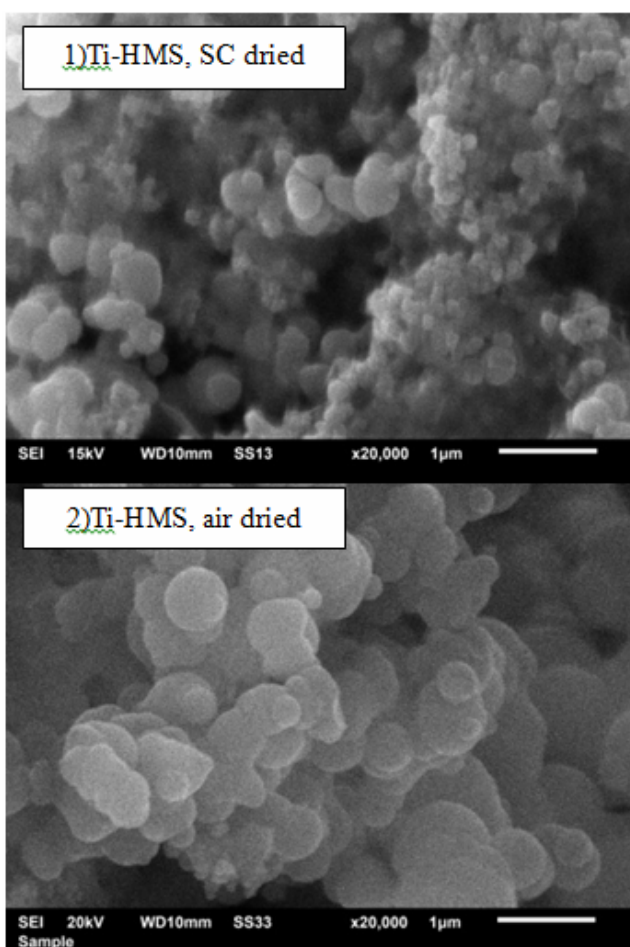
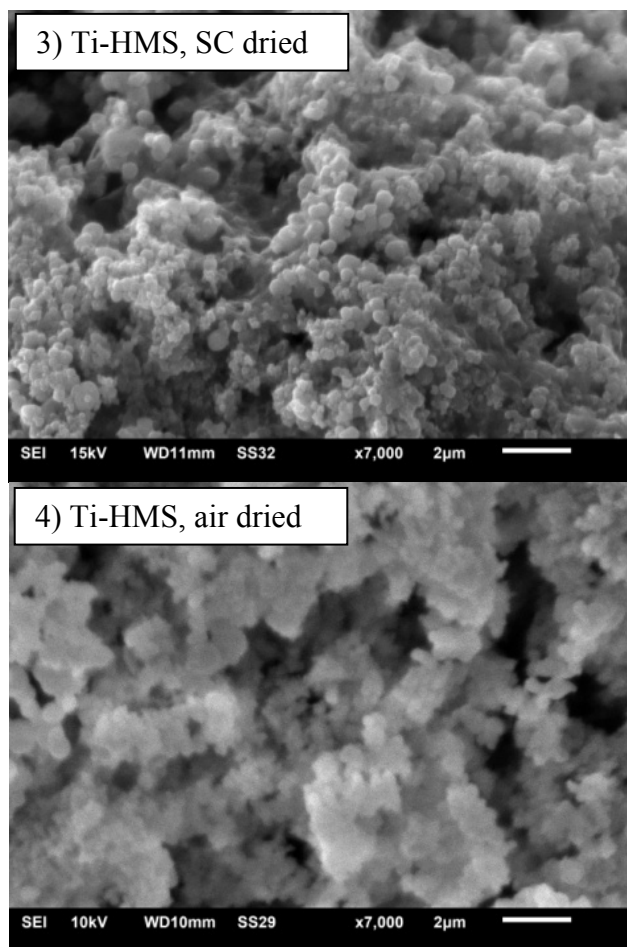


Figure 5. SEM images of calcined supports

Fig.6, reveal good Ti dispersion in both samples without observed anatase formation on the surface.

Concluding remarks

In the present work influence of drying procedure on textural characteristics of two Ti-HMS supports has been reported. The mesopores formation is obtained using dodecylamine as a structure directing agent. In polar solvent, DDA forms rodlike micels with hydrofobic tail oriented toward the center of the micel, and hidriphillic headgroup toward the micel/solvent interface.



The formation of mesostructure occurs via H-bonding interactions of precursors silanol hydrogens and electron pairs of the surfactant headgroups. The results for textural characteristics derived from nitrogen adsorption-desorption isotherms show significant improvement in mesopore volume and specific surface area of the support dried with supercritical solvent excess. Material with almost four times bigger mesopore volume is obtained with a supercritical process and with a much finer morphology. The formation of Ti-O-Si linkages is conformed with FT-IR spectroscopy, while the appropriate Ti dispersion is observed using SEM-EDS.

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Uticaj sušenja u višku natkritičnog rastvarača na teksturalne karakteristike nosača katalizatora Ti-HMS

Teksturalne karakteristike katalizatora i nosača katalizatora su od izuzetne važnosti kad je u pitanju korišćenje katalizatora u procesima u kojima učestvuju jedinjenja velike molekulske mase. Način sušenja vlažnog gela igra značajnu ulogu u očuvanju njegovih karakteristika. Heksagonalna mezoporozna silika (HMS) sa jonima titanijuma sve se više koristi kao nosač heterogenih katalizatora. U ovom radu je predstavljen uticaj sušenja u višku rastvarača u natkritičnim uslovima na teksturalne karakteristike Ti-HMS. HMS sa jonima Ti (Si/Ti atomskog odnosa 40) sintetisana je primenom sol-gel metode. Kao templejt za formiranje struktura korišćen je dodecilamin (S^o), a kao neorganski prekursori (I^o) tetraetilortosilikat (TEOS) i titanijum butoksid. Upoređene su specifična površina, mezoporoznost i zapremina pora nosača sušenog termičkom evaporacijom rastvarača u vazduhu i nosača sušenog u višku natkritičnog etanola. Rezultati pokazuju da je korišćenjem natkritičnog sušenja poboljšana vrednost specifične površine nosača i dobijena četiri puta veća vrednost zapremine mezopora.

Кljučне речи: katalizatori, mezoporozni katalizatori, sol-gel postupak, sušenje, frakcije nafte.

Воздействие сушки в избытке сверхкритического растворителя на текстурные характеристики носителя катализатора Ti-HMS

Текстурные характеристики катализатора и носителя катализатора имеют большое значение, когда речь идёт об использовании катализаторов в процессах с участием высокомолекулярных соединений. Метод сушки влажного геля играет важную роль в сохранении его характеристик. Шестиугольный мезопористый силикон (HMS) с ионами титана всё чаще используется в качестве носителя гетерогенных катализаторов. В настоящей работе представлено влияние сушки над растворителями (в избытке) в условиях сверхкритических напряжений на текстурные характеристики Ti-HMS. HMS с ионами Ti (Si / Ti атомное соотношение 40) синтезировали с использованием соль-гель-метода. В качестве матрицы для образования структур использовали додециламин (S^o) и в качестве неорганических предшественников (I^o) - тетраэтилортосиликат (TEOS) и буюксид титана. Сравнивали удельную площадь поверхности, мезопористость и объём пор носителя, высушенного путём термического испарения растворителя в воздухе, и носителя, высушенного в избытке сверхкритического этанола. Результаты показывают, что использование сверхкритической сушки улучшает значение удельной поверхности носителя и даёт в четыре раза большую величину объёма мезопора.

Ключевые слова: катализаторы, мезопористые катализаторы, соль-гель-процесс, сушка, нефтяные фракции.

Influence du séchage dans l'excès du solvant supercritique sur les caractéristiques texturales du support de catalyseur Ti-HMS

Les caractéristiques texturales des catalyseurs sont de première importance pour l'utilisation des catalyseurs dans les processus où participent les unités de grande masse moléculaire. Le mode du séchage du gel humide joue un rôle important dans la préservation de ses caractéristiques. Le silice hexagonal méso poreux (HMS) avec les ions de titane est de plus en plus utilisé comme le support des catalyseurs hétérogènes. Dans ce papier on a présenté l'influence du séchage dans l'excès du solvant dans les conditions supercritiques sur les caractéristiques texturales Ti-HMS. Le HMS aux Ti-ions (Si / Ti de ration atomique 40) a été synthétisé à l'aide de la méthode sol - gel. Le dodécyclamine (S^{10}) a été employé pour former les structures et TEOS et titane butoxide comme les précurseurs inorganiques. On a comparé la surface spécifique, la méso porosité et le volume des pores du support par l'évaporation du solvant dans l'air et le support séché dans l'excès de l'éthanol supercritique. Les résultats démontrent que la valeur de surface spécifique du support a été améliorée et on a obtenu la valeur du volume des méso pores quatre fois plus grande.

Mots clés: catalyseurs, catalyseurs méso poreux , procédé sol - gel, séchage, fractions de pétrole.