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REVIEW PAPER

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AEROGELS – II. Applications in catalysis

Sol-gel synthesis, and the resulting materials (xerogels and aerogels) are finding increasing application in the synthesis of catalysts, due to their unique characteristics. The most important features of the sol-gel process are: the ability to achieve homogeneity at the molecular level, the introduction of several species in only one step and the ability to stabilize metastable phases. The supercritical drying process produces aerogels with structural features quite different to conventional materials. Some of these characteristics of aerogels can make them very effective catalysts.

Due to the specific characteristics of sol-gel synthesis and the resulting materials (xerogels and aerogels) [1–14], there is a potential broad application of sol-gel synthesis in the manufacturing of catalysts. There are several critical parameters which determine the applicability of a successful catalyst. These parameters are: activity, selectivity, slow deactivation at the applied process conditions and good mechanical properties in the applied reaction system. In order to satisfy these criteria one must take into account the following catalyst properties during the design procedure: porosity, specific surface area, pore size distribution, surface chemical structure, active site distribution, active component particle size, stability of the material (thermal, chemical and mechanical) and catalyst particle size and shape. The advantages of sol-gel synthesis in catalyst preparations could be summarized as: the possibility of structure control on a molecular scale, the possibility of introducing several species in one step, which significantly reduces the complexity of the synthesis of complex catalytic materials and application of the kinetic constraints technique, which enables the stabilization of metastable phases [15].

SINGLE COMPONENT CATALYSTS

Although single component systems are rare in catalysis, considerable research has been conducted in this area. In the case of single component the catalysts, the catalytic properties have been adjusted during sol-gel synthesis. By variation of the sol pH, the relative rates of condensation and hydrolysis may be adjusted to obtain a catalytic material with the desired pore and surface chemical structure. Acid catalysed gels result in gels with micropores, surface water, surface silanol

groups and residual alkoxy groups, while base catalysed gels result in mesoporous gels with lower quantities of water, silanol groups and residual alkoxy groups. Another important parameter during sol-gel synthesis is the size of the alkoxy ligand, since it affects the relative rates of hydrolysis and condensation reactions due to steric and inductive effects.

Ko and coworkers have investigated the influence of the relative rates of hydrolysis and condensation by variation, on the porous structure of titanium oxide aerogel [16] and niobium oxide aerogel [17] type variation of the sol pH. In the case of a neutral sol, fast condensation results in rapid particle growth and very low porosity and specific surface area. When an acid catalyst was used, protonation of the functional group slowed down the condensation reaction, thus enabling enough time for the gel network to grow and the porosity to increase. Further addition of the acid slowed down the condensation further, resulting in a low porosity aerogel. Park and coworkers [18] have investigated the influence of acidity during sol-gel synthesis on the porous structure of titanium, zirconium and niobium oxide aerogels (dried using supercritical carbon dioxide). Their results indicate that increasing acidity of the sol leads, not only to an increase in the surface area, but also to decrease of the mean pore diameter. Wang and coworkers [19] have found that the selectivity of a sol-gel obtained alumina catalyst for the conversion of 2-propanol depended on the concentration of acid and basic catalytic sites. A selectivity shift towards acetone was observed in the case of base catalytic sites, while higher concentrations of acid catalytic sites (including pentacoordinated Al atoms) resulted in a selectivity shift towards isopropyl ether as the dominant reaction product. Ko and coworkers have compared the characteristics of niobium oxide xerogel and aerogel catalyst [20]. Their results indicate a different amorphous structure of the niobium oxide aerogel (remained amorphous even after heating up to 773 K) compared to the xerogel. An amorphous

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structure of this type of catalyst proved to be crucial in maintaining high levels of activity for acid catalysed reactions. The same group of authors has investigated the influence of the supercritical drying temperature on the obtained zirconium oxide, niobium oxide and titanium oxide catalysts [21,22]. In the case of zirconium oxide aerogel it has been shown that a higher supercritical drying temperature resulted in the crystallization of zirconium oxide, while in the case of niobium oxide a lower drying temperature resulted in the appearance of the crystal TT phase and the disappearance of Lewis acid sites (and an activity decrease for 1-butene isomerization).

MULTICOMPONENT CATALYSTS

This group of catalytic materials is much more abundant than single component catalytic materials, since working catalysts are typically very complex materials. The synthesis of multicomponent systems using sol-gel technology can improve existing catalytic materials and simplify their production. The conventional synthesis of catalysts usually consists of several steps which include: synthesis of the support, introduction of active species into the system and additional steps needed to prepare the catalyst in its final form. The sol-gel process, on the other hand, allows the introduction of several species in only one step and the materials obtained using the sol-gel process can have different end structures and catalytic properties compared to catalysts obtained using conventional techniques. With sol-gel obtained catalytic materials it is possible to preserve homogeneity at the molecular level, which is practically impossible with conventional techniques such as coprecipitation.

Oxide-oxide catalysts

Two oxides can be joined either as mixture of oxides or as two layers of different oxides. Mixtures of oxides are important catalytic materials since they exhibit acidic properties. The increased acidity of oxide mixtures is the result of homogeneous mixtures (M-O-M') at the atomic level. Conventional techniques of preparing of oxide mixtures (such as fusion and coprecipitation) are inadequate if high homogeneity is desired at the atomic level. The basic advantage of the sol-gel process in the synthesis of highly homogeneous mixtures lies in the opportunity of changing the relative reactivity of the precursors. Since both hydrolysis and condensation are nucleophilic substitution reactions, the relative reactivity of the precursors can be adjusted using: precursors with different alkoxy groups, prehydrolysis in the case of a less reactive precursor, slowing down the reaction of more reactive alkoxides by exchanging the alkoxy groups with other ligands and the application of different temperatures.

The synthesis of titanium/silica mixed oxide is a good example of the effect of prehydrolysis.

Scharml-Marth and coworkers have developed [23] a two stage process which consists of the incomplete hydrolysis of silicon alkoxide, followed by mixing with titanium alkoxide and finally completed by hydrolysis of the mixture. For comparison they produced a gel with identical composition, but obtained in only one step (a mixture of two alkoxides was hydrolyzed in one step). Structural investigation of the two gels (IR, Raman and NMR) revealed that in the case of one step mixture hydrolysis, the obtained gel consisted of titanium oxide particles surrounded by a silica matrix, while in the case of a two step process a highly homogeneous gel was obtained. The structural differences of these two gels were reflected in their catalytic behavior. The one step gel showed high activity as a support for vanadium active species in the reaction of NO reduction with NH₃ [24], since titanium oxide particles are good stabilizers of vanadium active species. The two step gel was inactive in this reaction, but showed very high activity as a catalyst in the reaction of 1-butene isomerization [25] due to its highly mixed structure and acidic properties.

Baiker and coworkers have investigated the catalytic properties of mixed titanium/silicon oxides in the reactions of epoxidation of olefins and allyl alcohols [26-33]. Their investigation included different gel types (xerogels and aerogels) and different supercritical drying conditions. The best catalytic properties were achieved with aerogel obtained using supercritical drying with carbon dioxide, due to its mesoporosity, structural stability and good titanium dispersion [26,27].

Aerogels and xerogels of silicon and vanadium mixed oxides were investigated as catalysts in the reactions of NO reduction [34,35]. The key parameters in achieving highly active catalysts were found to be: type of drying, vanadium content and vanadium precursor.

Beside titania/silica as a catalyst for 1-butene isomerization, a zirconia/silica was also investigated as a catalyst for the isomerization reaction [36]. This type of aerogel catalyst showed very high activity in the isomerization reaction due to the high surface concentration of Bronsted acid sites (the result of highly homogeneous oxide mixture).

Oxide-metal catalysts

Application of the sol-gel process in the synthesis of oxide-metal catalysts offers two possibilities: impregnation of the sol-gel obtained support with a metal compound or the introduction of a metal precursor directly in the sol-gel phase. The first type of synthesis is almost identical to the synthesis of oxide-oxide systems. The second one involves metal compounds in the sol-gel step. Unlike oxide precursors metal precursors, usually do not take part in the sol-gel chemistry, instead they are embedded in the growing gel network. Due to these differences in the sol-gel step, catalysts obtained using this procedure operate with

different catalytic properties and they exhibit different deactivation properties.

Azomoza and coworkers [37] have investigated Pt/SiO₂ catalysts obtained using sol-gel synthesis and the impregnation method. The sol-gel obtained catalysts (addition of metal precursors in the sol-gel step) had larger surface areas and specific structures of Pt particles. These particles were partially submerged into the SiO₂ gel network. Similar effects of submerged metal particles were observed for Ru/SiO₂ [38] and Pt/TiO₂ [39] catalysts.

Hoang-Van and coworkers have investigated alumina aerogels with Pd and Ce, Ba, and La oxides as catalysts for the treatment of engine exhaust gases [40,41]. These catalysts showed higher activity for CO oxidation and NO reduction under considerably lower temperatures than existing commercial catalysts.

Other catalytic systems

The sol-gel synthesis of catalytic materials enables the simple introduction of different chemical species into the system. The role of these species in the catalytic system can be diverse. One of the very interesting catalysts obtained using this strategy is the cogel zirconium-sulfate (solid superacid). Ko and coworkers have succeeded in producing this highly active solid superacid by the introduction of sulfuric acid in the sol-gel step [42-44]. Their results indicate that sulfate anions are trapped in the gel network at lower temperatures. After thermal treatment at elevated temperatures, beside the crystallization of zirconium oxide, the sulfate anions diffuse toward the gel surface. At the gel surface these anions are transformed into covalent sulfate structures with improved Broensted acidity. This type of catalyst showed very high activity for the isomerization of 1-butene. One of the key parameters of the catalyst activity was a high concentration of surface hydroxyl groups. Sulfuric acid concentrations leading to greater than monomolecular layers on the catalyst surface lowered the catalyst activity, while platinum was used as a good stabilizing agent for surface sulfate ions [45-47]. Another similar active isomerization catalyst was found to be zirconium-phosphate aerogel [48].

Zirconium aerogels were investigated as catalysts for methanol synthesis [49]. Zirconium-copper catalyst was obtained using one step sol-gel synthesis and the highest activity in methane synthesis was observed using a catalyst dried with supercritical carbon dioxide.

Alkylation catalysts

Alumina/silica with zinc chloride aerogels were found to be highly active catalysts for the alkylation reaction [50]. Supported metal halides, particularly zinc chloride, have been investigated as catalysts for Friedel-Crafts alkylations in recent years. The most widely studied material, zinc chloride supported on

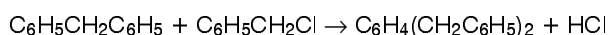
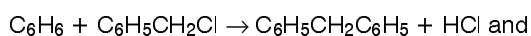
Montmorillonite K10 (Clayzic), was first reported in 1989 [51]. Since the original report, a number of studies have investigated the reasons for the remarkably high activity of this material, and have widened the range of alkylation reactions for which the Clayzic is an effective catalyst [52-58]. These studies have revealed certain important characteristics of the catalyst: Clayzic contains both Broensted and Lewis acid sites [53,56,57], there is little residual lamellar structure in the catalyst [54,56], the activation temperature for Clayzic critically affects its alkylation catalytic activity [56,58] and catalysts with a pore size distribution centered around 5-6 nm pore radius exhibit the highest levels of catalytic activity [55]. The sol-gel synthesis of an alumina/silica with zinc chloride alkylation catalyst and its characterisation was first reported in 1997 [59]. The one step sol-gel derived xerogel catalyst and catalyst obtained by impregnation of the sol-gel derived alumina/silica xerogel support with zinc chloride, showed considerably higher levels of catalytic activity in comparison to Clayzic. The most active xerogel catalysts showed relatively high levels of framework aluminium species compared to the non-framework sites, and also had higher surface areas and pore volumes than the catalysts with lower activity.

The aim of the study of an aerogel alkylation catalyst was to investigate the influence of supercritical drying conditions and aerogel structure on the Friedel-Crafts alkylation catalytic activity. Catalytic aerogels were obtained by one step sol-gel synthesis and subsequent supercritical drying of the wet gel with supercritical carbon dioxide. Aerogel catalyst samples were characterized by BET nitrogen adsorption, FTIR spectroscopy and atomic adsorption spectroscopy. The Friedel-Crafts alkylation products were analyzed by gas chromatography. The benzylation of benzene with benzyl chloride was used as an alkylation test reaction.

The sol-gel synthesis was performed according to Miller et al. [59]. Anhydrous zinc chloride (ACROS), 1-butanol (MERCK), and tetraethoxy orthosilane - TEOS, aluminium tri-sec-butoxide and benzyl chloride (all FLUKA) were used as reagents. Aluminium tri-sec-butoxide (9.84 g, 0.04 mol) was mixed with 1-butanol (100 cm³) and then TEOS (8.32 g, 0.04 mol) was added. The mixture was stirred vigorously and heated to 343 K for 5 minutes until a clear solution was obtained. The solution was cooled down to room temperature. Then, it was hydrolysed with water (18.75 cm³, 1.04 mol) containing dissolved zinc chloride (3.75 g, 0.025 mol). The solution was stirred for 15 min and left to stand overnight (gelation). Water and a certain amount of excess 1-butanol were then removed by heating the gel to 423 K, and (after which) a "thickened" wet gel was obtained. The above procedure describes the wet gel synthesis of samples with the ratio Al/Si=1. For the sample with Al/Si=3, the amounts of aluminium tri-sec-butoxide and TEOS were changed accordingly, while the other conditions maintained as described.

The "thickened" wet gel sample, typically 12–14 g, was dried in a 70 cm³ tubular extractor (Autoclave Engineers SCE Screening System), with supercritical carbon dioxide. In all the supercritical drying (SCD) experiments, the flow rate was maintained at 90 gCO₂/h for 4 h.

In a typical catalyst testing procedure, benzene was stirred with a freshly activated catalyst sample. Prior to the catalyst activity tests, the catalyst samples (315–800 μm fraction) were activated by heating in an oven at 458 K for 2 h. An aliquot of benzyl chloride was then added and the reaction mixture stirred for 15 min at 298 K. The mass ratios of the reactants and catalyst were: benzyl chloride/catalyst = 10 and benzene/benzyl chloride = 3.5–4. An excess of benzene resulted in the formation of diphenyl methane as the dominant product:



The catalyst was removed from the reaction mixture by filtration and the mixture was analyzed by gas chromatography. The conversion of benzyl chloride (XB, %) was defined as the total molar conversion of benzyl chloride to diphenyl methane and the ortho-, meta- and para-isomers of dibenzyl benzene.

The supercritical drying conditions, Al/Si ratio, zinc chloride content, surface area, total pore volume and benzyl chloride conversion of different aerogel catalyst samples are shown in Table 1. The supercritical drying conditions considerably influence the structure and catalytic activity of the aerogel catalysts (catalyst samples AG1, AG2 and AG3). The pressure and temperature conditions of the supercritical carbon dioxide used in the drying experiments, resulted in different supercritical carbon dioxide densities. The zinc chloride leaching studies have revealed that higher carbon dioxide densities had resulted in the removal of zinc chloride from the aerogel catalyst surface (AG1 and AG3) by extraction with supercritical carbon dioxide. The lower zinc chloride content of catalyst AG3 compared to

Table 1. The Al/Si ratio, SCD conditions, zinc chloride content, surface area, pore volume and conversion of benzyl chloride in the benzylolation of benzene (XB) of different aerogel catalyst samples.

CATALYST	AG1	AG2	AG3	AG4
Al/Si ratio	1	1	1	3
SCD temperature, K	313	498	498	498
SCD pressure, bar	100	100	200	100
SCD CO ₂ density, kg/m ³	647	114	236	114
ZnCl ₂ content, weight %	28.29	39.64	25.80	37.45
Sa, m ² /g	176	139	162	131
Vp, cm ³ /g	1.041	0.950	1.284	1.087
XB, %	41	53	13	64

AG1 could be explained by the improved zinc chloride diffusivity in supercritical carbon dioxide at higher temperatures [60].

The supercritical drying conditions influenced the porous structure of the obtained aerogels, as indicated by the surface area, total pore volume (Table 1) and pore size distribution (Figures 1 and 2). The surface area and total pore volume of the catalysts with lower zinc chloride content (AG1 and AG3) are increased compared to the catalyst with higher zinc chloride content (AG2), and a general shift of pore sizes to larger pore radius is observed for the catalysts with lower zinc chloride content. The pore size distributions of AG1, AG2 and AG3 are broad, with peaks at around: 8.2 nm pore radius for AG1, 4 nm pore radius for AG2 and 2.8 and 6 nm pore radius for AG3. These differences in the porous structure of the investigated samples are expected due to the extraction of zinc chloride from the aerogel surface. However, if the difference in total pore volume of AG3 and AG2 is compared to the calculated lost volume of zinc chloride (calculated from the weight difference of zinc chloride in both samples and the zinc chloride density at 298 K), the pore volume increase is significantly higher than the expected one (the observed difference is 0.334 cm³/g and the expected one 0.048

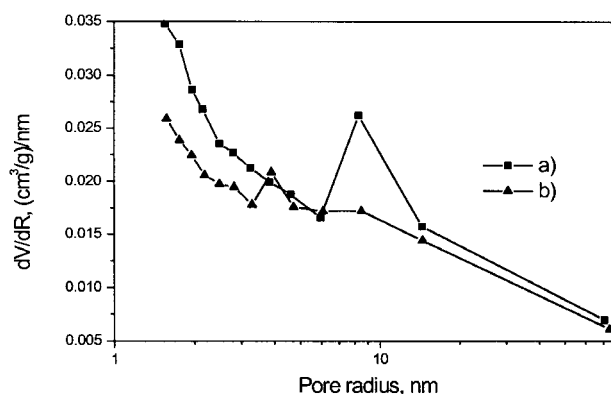


Figure 1. Pore size distribution of: a) aerogel catalyst AG1 and b) aerogel catalyst AG2.

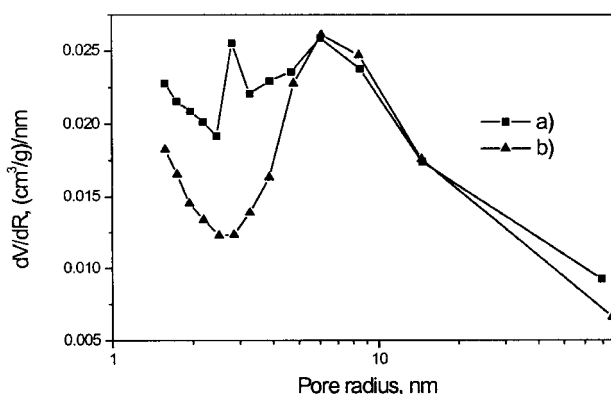


Figure 2. Pore size distribution of: a) aerogel catalyst AG3 and b) aerogel catalyst AG4.

cm³/g). If catalysts AG1 and AG2 are compared, a similar difference between the observed and the expected pore volume change is observed. This could be explained by the influence of the different drying conditions on aerogel porous structure or/and by the presence of highly polar mesopores which are too polar to allow ingress of the non-polar nitrogen adsorbate [56] and which, therefore, are not being recorded by BET nitrogen adsorption measurements.

FTIR spectra of aerogel samples obtained under different supercritical drying conditions, are shown in Figure 3. The band at about 1100 cm⁻¹, attributed to the Si-O stretching vibration [61,62], shifts to lower wavenumbers: 1054 cm⁻¹ for AG1, 1064 cm⁻¹ for AG2 and 1079 cm⁻¹ for AG3. Other characteristic bands are: a band at about 460 cm⁻¹ attributed to Si-O bending, a broad one centered at about 600 cm⁻¹ attributed to octahedral Al-O a band centered at about 710 cm⁻¹ attributed to tetrahedral Al-O, and a shoulder at about 890 cm⁻¹ attributed to tetrahedral Al-O [61]. A shift of the Si-O stretching vibration absorption band from 1100 cm⁻¹ to lower wavenumbers indicates the presence of Al-O-Si bonds [61-63] in the investigated samples. The value of the Si-O stretching vibration band shift decreases from AG1 to AG3, thereby indicating that high temperature and pressure during supercritical drying result in alumina/silica network separation into Al-rich and Si-rich phases.

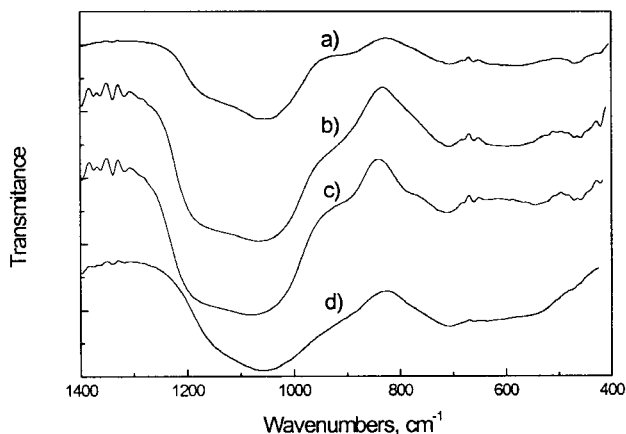


Figure 3. FTIR spectra of aerogel catalysts: a) AG1, b) AG2, c) AG3 and d) AG4.

Different supercritical drying conditions resulting in different aerogel composition and structure, considerably influence the catalytic activity of the obtained aerogel catalysts. The catalysts with lower zinc chloride content are, as expected, less active in the benzylation of benzene (AG1 and AG3) compared to the catalyst with higher zinc chloride content (AG2), due to the insufficient surface coverage with zinc chloride [59,64]. Although the zinc chloride content of AG1 is only slightly higher than that of AG3, the activity decrease is much

more pronounced for AG3. A systematic investigation of the influence of pore size distribution on the catalytic activity for a similar catalytic system (Clayzic and Silizic) [55] showed that the maximum activity was observed for catalysts with a pore size distribution centered around a 5-6 nm pore radius. Pores with larger radii than optimal were found to be still active for alkylation, while those with smaller radii than optimal were found to be significantly less active. Based on the zinc chloride contents and pore size distributions of AG1 and AG3, similar catalytic activity of these two catalysts is expected, since the more favourable pore size distribution of AG3 should counterbalance its lower zinc chloride content. However, this is not the case. If the FTIR spectra of these two catalysts are compared, a higher degree of Al-O-Si bonding is observed in AG1, while the alumina/silica network of AG3 is largely separated into Al-rich and Si-rich phases. As mentioned earlier, the most active xerogel catalysts were found to show relatively high levels of framework aluminium species compared to non-framework sites [59]. The significantly higher catalytic activity of AG1 compared to AG3 confirms that the aerogel catalyst activity is strongly influenced by the degree of Al-O-Si bonding in the alumina/silica network. A higher degree of Al-O-Si bonding enhances the catalytic activity of the corresponding aerogel catalyst.

The influence of pore size distribution centered around the 5-6 nm pore radius and the degree of Al-O-Si bonding on the catalytic activity of the aerogel catalyst, is further demonstrated by the catalytic activity of the AG4 catalyst. This aerogel was obtained using a different Al/Si ratio in the sol-gel step (Al/Si=3), and with the other conditions of the sol-gel step identical to those used for the preparation of the other aerogel catalyst samples. Low density supercritical carbon dioxide was used in the drying procedure in order to preserve a sufficient quantity of zinc chloride on the catalyst surface. The pore size distribution of this catalyst was centered around a 6 nm pore radius (Figure 2) and the Si-O stretching vibration band was shifted to 1055 cm⁻¹ (Figure 3) indicating the high degree of Al-O-Si bonding in the alumina/silica network. Although catalysts AG4 and AG2 have similar zinc chloride contents, the pore size distribution centered around 6 nm and the higher degree of Al-O-Si bonding result in the higher catalytic activity of catalyst AG4.

It may be concluded for the alumina/silica with zinc chloride aerogel alkylation catalyst that:

- the obtained aerogel catalyst is active in the benzylation of benzene with benzyl chloride,
- the supercritical drying conditions influence the structure and catalytic activity of the aerogel catalysts,
- the higher density of supercritical carbon dioxide during the drying procedure results in catalysts with lower zinc chloride content due to zinc chloride extraction,

larger surface areas, larger total pore volumes and lower catalytic activity,

- the higher drying temperature and pressure cause separation of the alumina/silica network into Al-rich and Si-rich phases,

- the zinc chloride content, pore size distribution and degree of Al-O-Si bonding in the aerogel network influence the catalytic activity of the aerogel catalysts and,

- the pore size distribution centered around a 6 nm pore radius and a higher degree of Al-O-Si bonding in the aerogel network, were found to increase the catalytic activity of the corresponding aerogel catalyst.

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IZVOD

AEROGELI – II. Primena u katalizi

(Pregledni rad)

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Sol-gel sintezom se dobijaju materijali specifičnih strukturnih osobina: kserogelovi i aerogelovi. Zbog svojih specifičnih strukturnih osobina ovi materijali, kao i sol-gel sinteza, potencijalno su široko primenljivi u oblasti katalize. Osnovne osobine sol-gel sinteze koje omogućavaju dobijanje katalitičkih materijala su: mogućnost uvođenja više hemijskih vrsta u jednom stupnju, mogućnost dobijanja materijala homogenih na molekulskom nivou, mogućnost podešavanja relativnih brzina reakcija hidrolize i kondenzacije što može da se iskoristi za podešavanje krajnje strukture materijala, kao i mogućnost stabilizacije metastabilnih faza. Osim toga je što je sol-gel sintezom moguće dobiti materijale visoke homogenosti i sasvim posebnih strukturnih osobina, sama sinteza omogućava i smanjivanje ukupnog broja stupnjeva koji rezultuju katalitičkim materijalom. Metodom natkritičnog sušenja se iz gelova dobijaju aerogelovi. Korišćenjem metode natkritičnog sušenja se mogu dobiti materijali koji imaju znatno uvećanu poroznost u odnosu na materijale dobijene metodama klasičnog sušenja. Aerogelovi mogu posedovati i sasvim specifične strukture same mreže gela koje se mogu sresti kod kserogelova. Natkritičnim sušenjem sa ugljen dioksidom, dobijaju se aerogelovi sa visokim nivoom koncentracije aluminijumovih atoma sa koordinacionim brojem 5. Ove strukture su poznate po svojoj Lewis-ovoj kiselosti što ih čini interesantnim za primenu kod kiselo katalizovanih reakcija kao što je alkilacija.

Key words: Sol-gel synthesis • Aerogels • Catalysts • Alkylation aerogel catalyst •

Ključne reči: Sol-gel sinteza • Aerogelovi • Katalizatori • Aerogel katalizator za alkilacije •

