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COATING OF POLYMERIC SUBSTRATE CATALYSTS ON METALLIC SURFACES

This article presents results of a study on coating of a polymeric substrate catalyst on metallic surface. Stability of coating on metallic surfaces is a proper specification. Sol-gel technology was used to synthesize adhesion promoters of polysilane compounds that act as a mediator. The intermediate layer was coated by synthesized sulfonated polystyrene-divinylbenzene as a catalyst for production of MTBE in catalytic distillation process. Swelling of catalyst and its separation from the metal surface was improved by i) increasing the quantity of divinylbenzene in the resin's production process and ii) applying adhesion promoters based on the sol-gel process. The rate of ethyl silicate hydrolysis was intensified by increasing the concentration of utilized acid while the condensation polymerization was enhanced in the presence of OH⁻. Sol was formed at pH 2, while the pH should be 8 for the formation of gel. By setting the ratio of the initial concentrations of water to ethyl silicate to 8, the gel formation time was minimized.

Key words: polymeric substrate catalysts; surface coating technology; adhesion promoters.

Coating of metallic and ceramic surfaces by polymers has been used for various applications such as production of catalysts. Spes research team made the first attempt by coating ceramic packings with a polymer acting as catalyst [1]. This work encountered the following problems: *i*) difficulties in control of the polymer sintering temperature, *ii*) decreasing of the catalytic activity of the produced resin and *iii*) very low mechanical stability of the produced catalytic packings. Later, catalytic packings in the form of Raschig rings were synthesized by the Rehfinger research team [2]. Their process was based on polymerization of a monomer using pore-forming agents. The properties of the produced samples were comparable with commercial ones except that their mechanical stability was low. Afterward, Kunz and Hoffmann placed ion-exchange resins in pore volumes of ceramic substrates [3]. They added ceramic rings to a polymerization reactor of an ion-exchange resin. In the next step, sulfonation process was performed over the resin that covered the rings. The mechanical property of the pro-

duced catalytic packings was weak. They were brittle and could not be loaded in processing systems.

Catalytic packings have been widely used for production of various chemicals through various processes such as reactive distillation. In a reactive distillation system, both processes of reaction and distillation are performed simultaneously in a single column. This process benefits the following advantages: *i*) overcoming of existing reactions-equilibrium limitations, *ii*) presenting higher selectivity and *iii*) reducing of operational expenses. In production of some chemicals based on this process such as methyl tert-butylether, MTBE, ion-exchange resins are used as catalyst. Commercial ion-exchange resins are small beads that cannot be directly used in reaction-distillation columns. Usage of resins in this form results in rising of the columns pressure drop, and their holdup [4-7].

In order to cope with this problem, this research was performed to produce catalytic packings that have proper properties. Stability and strength of these catalyst coatings were promoted by using sol-gel process for synthesis of mediator compounds such as vinyltriethoxysilane. Based on this method, the produced consolidated packings with ion-exchange resin maintained their initial strength in high temperature conditions and presence of various solvents. However this study was performed over one type of product, but the importance of this research is its general-

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zation for numerous applications on coating of different materials over metals.

THEORY

Adhesion promoters

Early application of adhesion promoters' agents could be referenced to the mid-1950s. These materials were silane compounds with amine groups. They were designed to overcome weak adhesiveness of phenolic resins on fiber glass compounds. Silane compounds could be addressed as the first adhesion promoters. Vinylsilane is used for adhering of polyester resins to different compounds. Later on, they were extended by synthesis of chromic complex compounds for utilizing on glass substrate materials. Basic improvements in this field were obtained by introduction of methacrylate silane for increasing the adhesion strength of polyester compounds on glass fibers. In the early 1970s, numerous theoretical and experimental studies were performed on chemistry of silanes and their production technology. Later on, usage of strengthened silane was commercialized and the quality of produced materials was improved. During the 1970s, undesired effects of water on strength of coating cohesions were studied that result in improving of the quality of adhesion promoters. Also, studies on a set of new adhesion promoters including various compounds of titanium and zirconium were performed. Recently, components of zircoalominate were significantly used as industrial surface coatings while the silane components were constantly used due to their lower cost.

Adhesion of organic coatings to surface of materials has various usages such as protection of materials. An organic surface coating must be perfectly adhered to the surface material and sustain its adhesiveness under various conditions. However, there are some organic coatings which lose their adhesiveness very fast upon their exposure to humid environment, or floating in water. The importance of coatings' adhesiveness for protection of material against corrosion in humid environments was studied by Funke [8].

There are various techniques for preparation of surfaces that have the highest adhesiveness. Some of the major methods are: *i*) excretion of polluting of surfaces, *ii*) changing of surfaces profile and *iii*) modification of their chemical structure such as phosphating of steel and aluminum anodic operations. Adhesion promoters are known as coupling agents that can make basic bonds with the substrate, organic surface coating, or both of them. Some physical properties of these bonds are their hardness and strength

against humidity that are measurable. A main practical and essential problem on the usage of adhesion promoters is lack of experimental and numerical data for the bond strength.

Sol-gel processing of silane compounds

Formation of silica-gel on various materials including metals was proposed in 1982. Afterward, a variety of studies has been done in the field of formation of sol-gel. One of them was production of low density silica-monoliths in which their drying process was performed at super-critical point. The usage of silane compounds in production of sol-gel has made a significant improvement in the field of surface coatings. Results of initial tests have proved that hydrolysis of tetra-ethyl-ortho-silicate under acidic conditions produces glassy SiO_2 . One application of this founding was coating of silica on window vents that result in reduction of heat losses. Fast drying of the produced silica-gel by this method made its construction structure weak and brittle. Thus, for preventing fragmentation and powdering of the produced silica-gel, the drying time must be in the order of one year. This made the process tedious and consequently it remained untouched for years.

Roy produced smooth chemical surfaces based on sol-gel method [8,9]. He used colloid gels and gained various compounds of ceramic including Al, Si and Zr. The morphology and granularity of produced particles can be controlled based on this innovation. The final size of silica powders is a function of initial concentrations of water and ammonia, type of functional groups adhered to silane, and reaction temperature. Materials produced by this method have higher purity and homogeneity. The temperature of reaction in this method is low in comparison to other approaches.

The first international conference in the field of production of materials in the form of sol-gel was held in 1984. It was devoted to discussions and reviews on production of new and high quality materials for various applications. But the manufacturing details of most of these materials were kept secret due to their application in atomic and aerospace industries. Generally, the aim of the production of materials based on sol-gel technology is control of their surfaces and interfaces during formation process. Control of surface gradient and production of materials with unique physical properties by inorganic and organic materials are other objectives of sol-gel formation. Accuracy of calculations and analytical techniques in the scale of nanometer is an important factor throughout of sol-gel formation. Improvements have been gained by per-

forming of researches in the field of sol-gel such as reduction on the time of drying from a period of one year to only few days. Another existing problem in the sol-gel process is the breaking down of products due to volume reduction of the produced materials during drying. The following methods exist for production of sol-gel monoliths [10,11]:

a) Formation of gel by using of colloidal solutions of powders.

b) Hydrolysis and condensing polymerization of materials composing nitrate or alcoxide. The drying process of the produced gels has performed under supercritical conditions.

c) Hydrolysis and condensing polymerization of new materials such as alcoxide. The drying process of products has done at atmospheric pressure.

Basically, sol is formed by dispersion of colloidal particles in a liquid with sizes in the range of 10 to 100 nm. Gels contain internal bonds which form a rigid network with a pore size in the order of few micrometers. The average length of polymeric chains is greater than 1 μ m. The term of gel covers various materials. Their structure can be classified in four following groups:

a) Regularly layered structure.

b) Polymeric network based on shared electrons.

c) Polymeric network formed by physical aggregation of materials with relatively high irregularity.

d) Completely irregular structure.

Gel from silane compounds may be formed by growth of a network of separate colloidal particles. It could be formed in a three dimensional network shape with internal bonds *via* two simultaneous processes of condensing polymerization and hydrolysis. By removal of the inter-cellular liquid of gel in the form of vapor under supercritical condition, its network has not destroyed and forms a low density gel that is called aerogel. Pore volume of these gels was more than 98% and their density is less than 80 kg/m³. The gel was instantly condensed by thermal treatment under atmospheric conditions. This process removes the gel's inter-cellular liquid. These types of gels are named xerogel. Alcogel is a common name for the gels that alcohols are a part of inter-cellular liquid. Principally the term of gel is usually used for both types xerogel and alcogel. Dried gels lost all of physically absorbed liquid. The drying process occurs at temperatures within the range of 100 to 180 °C.

For pores with small radius, the capillary pressure of liquid during drying of gel can be determined by the relationship $\Delta p = 2\gamma(\cos\theta)/r$, where Δp represents pressure difference in capillary tubes, θ is the contact angle, γ denotes the surface energy in the va-

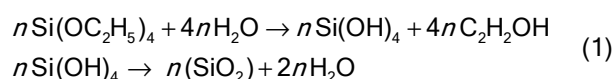
por-liquid interface, and r indicates the pores radius. In a dried gel, there are high concentrations of absorbed chemicals, such as hydroxyl over the gel pores' surface. Thermal treatment of gels at temperatures within the range of 500 to 800 °C can repulse hydroxyl groups. Furthermore, this process reduces the contact angle θ , and the sensitivity of gels for re-absorbing of water. This results in completely stable gels. Thermal treatment of a gel at high temperatures reduces its pores number which is named condensing. In this phase, the density of monoliths is increased, but the pores volume ratio is decreased. In fact, porous gels are condensed to a glassy phase. The condensing operation for produced gels based on the first method is performed at temperatures within the range of 1250 to 1500 °C, while the third method is carried out at a temperature of 1000 °C.

EXPERIMENTAL

Theoretical studies on hydrolysis of ethyl-silicate

Hydrolysis of tetra-ethoxy-silane has been used in various industries such as production of silica glue. The hydrolysis process was done in the presence of acidic or basic catalyst. Due to the immiscibility of water and ethyl silicate, a mutual solvent for the production of homogeneous reaction was used. This section discusses the formulation of reactions for ethyl silicate hydrolysis, the hydrolysis rate, and production rate of silica-gel.

Hydrolysis of ethyl silicate and dehydration of reaction product can be shown as follows:



Degrees of the reactions' conversion are related to following conditions:

a) Total amount of lost water (L_T), that is equivalent to the difference of taken water by the first reaction and produced water by the second reaction.

b) Production of alcohol (L_H), that corresponds to the amount of used water by the first reaction.

c) Degree of monomer conversion.

where L_T and L_H are mole of water or alcohol per mole of ethyl silicate.

A simple equation in each phase of the reaction can be written in the form:

$$L_T = L_H - \frac{aL_H}{2}$$

where parameter a is the degree of conversion in the second reaction.

By determination of L_T and L_H the conversion rate of both reactions and the number of unreacted hydroxyl groups can be determined. Thus, an average percent of formed polyethoxysiloxane can be calculated through measurement of monomer conversion.

Sol-gel processing of ethyl-silicate

Carl-Fischer titration method is a standard method for measurement of water content by volumetric accuracy of 1%. The method was applied to measure the moles of water in the reaction contents at two distinct time of t and t_0 , namely M_t and M_0 . Thus:

$$L_T = \frac{M_{t_0} - M_t}{S_{t_0}} \quad (2)$$

where S_0 is the initial concentration of silicate in mol/L.

The amount of formed alcohol cannot be measured through hydroxyl groups based on direct chemical methods, as all products have the same chemical group. Therefore, initially the produced alcohol was separated by distillation of the produced mixture in vacuum through a vacuum rotary apparatus. Concentration of ethyl-alcohol in the mixture, c_b , was determined by density and related indices. Considering c_t to be measured by weight percent, then:

$$L_H = \frac{m_d - (M_t V_m \times 18.02) / 1000}{V_m} \times c_t \times \frac{1000}{S_{t_0} \times 46.07} \quad (3)$$

where V_m and m_d are volume of the mixture before distillation, and the distilled mass, respectively. By presenting the mass of used silica by m , the moles of unreacted ethyl-silicate becomes:

$$\frac{1000m}{60.06V_m S_{t_0}}$$

RESULTS AND DISCUSSION

The experiments were performed in a batch reactor while dioxane was used as a solvent. Concentrated hydrochloric acid, 12 M, was used as a catalyst for the hydrolysis reaction. However, it should be mentioned that usage of other strong acids or bases achieves a similar result. Gel was formed as acid was slowly added, drop by drop.

The gel formation time *versus* the ratio of water concentration to ethyl silicate concentration is illustrated in Figure 1. As shown, the lowest gel formation time occurred for the ratio of 8.

The reaction of hydrochloric acid and ethyl silicate is exothermic. The rate of reaction is reduced by using low concentration acid in a low pH reaction environment. Under this condition, the amount of L_H can be determined. Results are shown in Table 1.

During formation of silica-gel, the produced samples were poured into molds of a particular shape. Then, ammonium hydroxide was used for setting the pH to 2. Samples were stored at a temperature of 20 °C for one day. Under this condition the produced gels were totally floated in liquid and the condensation polymerization process was performed further. The reaction enhances the gels' strength, and keeps them from damaging during the drying process. At the same step, the formed gels were placed in a furnace at 120 °C for a period of 6 days. During this period, the weight and temperature of samples were fre-

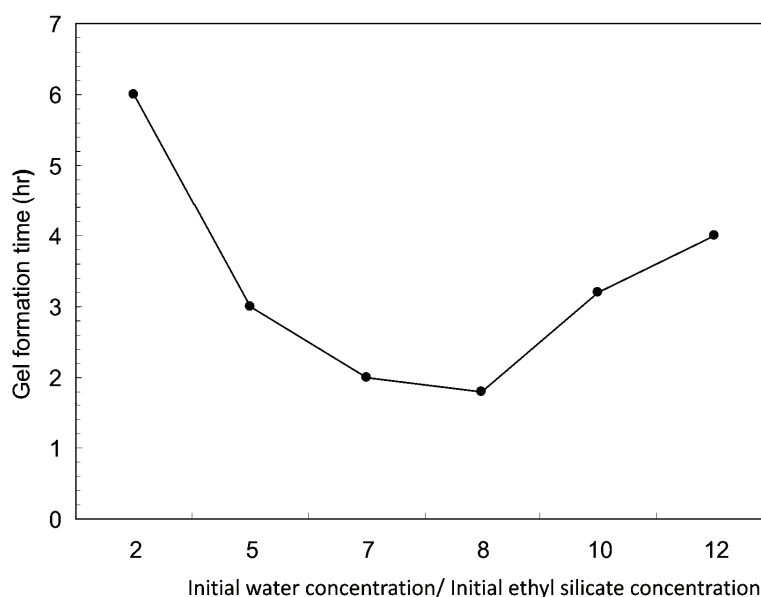


Figure 1. Variation of gel formation time with ratio of the initial concentrations of water to ethyl silicate.

Table 1. Hydrolysis of ethyl silicate by dioxane solvent at 25 °C

Experiment No.	HCl, mol/L	Ethyl silicate, mol/L	H ₂ O, mol/L	Water/ethyl silicate
1	0.1575	0.19	1.43	7.4
2	0.0702	0.2	1.59	7.7
3	0.0132	0.21	1.47	6.8
4	0.004	0.20	1.20	5.7
5	0.00005	0.21	1.24	5.8
6	Distillated water	0.22	1.35	6.1

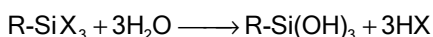
quently measured for calculation of their contents' variations. Then, the samples were transferred into a furnace at 600 °C for removal of existing silanol bonds (Si-OH) from the pores of gels. In this stage, highly porous gels with high surface area were produced. This dewatering phase is also named chemical stabilization. During this phase, Si-O bonds were formed as basis for surface coating of various materials such as iron, aluminum, ceramic, and alumina. Performing of process in the presence of mineral salts such as 0.05 M NaCl multiplies the diameter of generated pores. These are a suitable substrate for coating of catalysts. To prepare metallic surfaces for coating by silica-gel, a set of special operations must be performed.

Production of silica sol-gel on aluminum and alumina

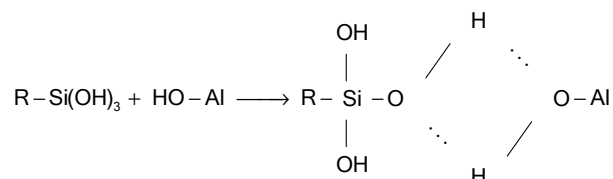
For production of silica sol-gel on aluminum and alumina, the explained process stages in production of sol-gel in previous sections were repeated with one difference. The only difference was inserting aluminum into the reactive environment in order to form the produced silica-gel over the metallic surface. This prepares the surface of the aluminum for placing of the producing catalyst, sulfonated polystyrene-divinylbenzene, over it. In this stage, various compounds of vinyl and silane such as vinyl triethoxy silane was used for production of silica sol-gel, since vinyl derivatives have adequate strength for setting of chemical bonds to the catalyst. Furthermore, spherical particles of α -alumina were used as substrate material without any additional process, as these particles are totally neutral, consistent, and nonpoisonous for coating of silica-gel.

After production of sol-gel triethoxysilane in presence of α -alumina, the hydrated silanol makes bonds with group of Al-OH on the surface of aluminum oxide. Water is produced as a result of the bond making process. In this reaction, hydrogen bonds could be produced upon drying condition. Possible reactions between α -alumina and vinyltriethoxysilane are shown in following section which R and X represent vinyl and ethoxy groups, respectively.

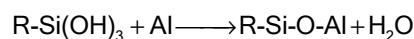
1) Hydrolysis of esteric group:



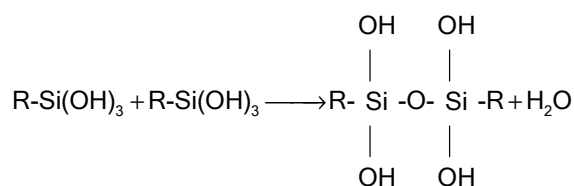
2) Hydrogen bond to the surface:



3) Condensation reaction on the surface:



4) Condensation polymerization of silane:



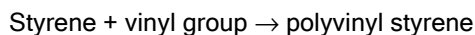
As shown in the reactions, the vinyl group has no effect on hydrolysis and condensation polymerization reactions. Infrared spectroscopy was implemented for study of formed silane films structure over aluminum's surface.

Preparation of aluminum - ion exchange resin packings

Based on the performed infrared spectroscopy results, vinyl groups of vinyltriethoxysilane did not participate during the hydrolysis and condensation polymerization. The vinyl groups remained in their initial form and according to the presented mechanisms can react with polystyrene-divinylbenzene. In this section, the method of adding catalytic resin for production of aluminum-silica-gel is described in detail.

Initially, 80 g styrene and 20 g divinylbenzene, DVB, were added into a batch reactor. Then, 1 g benzylperoxide as an initiator, 5 g normal hexadecane, and 5 g normal octadecane were added as pores formation agent. The mixture was stirred for 10 min and aluminum particles with coating of silica-gel were inserted in the reaction's contents. In the next step, for further polymerization, the temperature of the mixture was increased to 90 °C and was kept at it for a period of 3 h. Then, the coated aluminum particles that were

coated with a film of polystyrene-divinylbenzene ion exchange resin were removed from the reactor and were cooled. Chemical bonds between silica-gel and produced ion exchange resin were formed through existing vinyl groups in silica-gel. This could be shown in following form:



The thickness of formed films over aluminum-silica-gel was directly depending on the immersing time of aluminum in monomer mixture. Since the coated aluminum particles with ion-exchange resin act as catalyst, their surface area and pore volume are important properties. Figure 2 shows variation of measured

surface area with respect to polymerization time in presence of 20% divinylbenzene. Furthermore, variation of measured pore volume versus polymerization time in presence of 20% divinylbenzene is depicted in Figure 3.

The coated samples were sulfonated by placing them in concentrated sulfuric acid at temperature of 100 °C for several hours. The produced samples were washed and dried at 100 °C.

Pore volume of formed siloxane of the produced sample during various stages of sol-gel formation was measured. Figure 4 shows the variation of the pore volume of formed siloxane during the process. As shown, the pore volume of the produced films is much

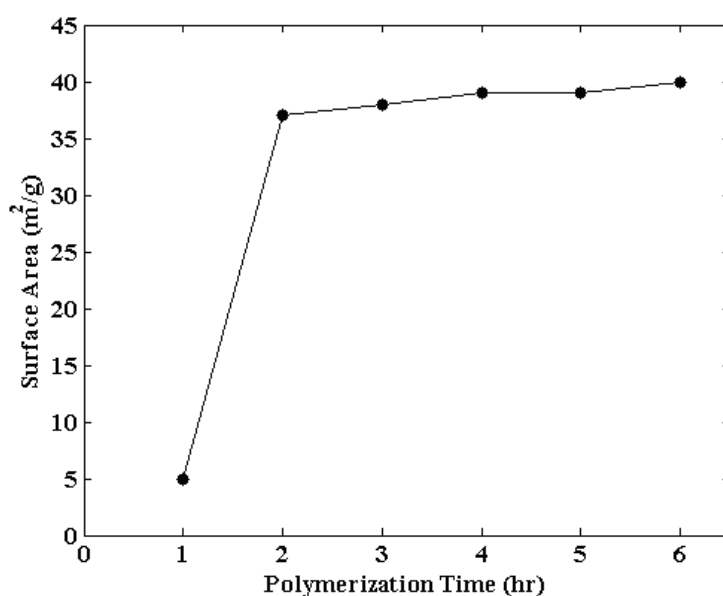


Figure 2. Variation of surface area of the ion-exchange resin versus polymerization time for 20% DVB.

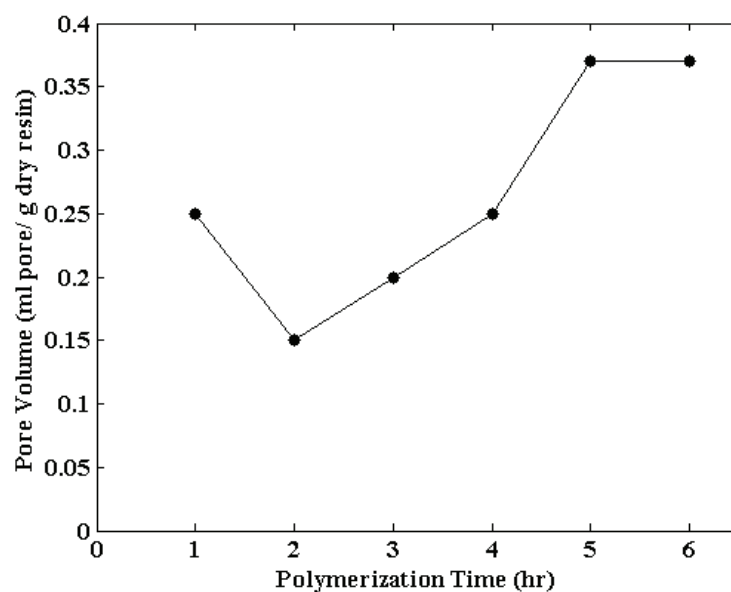


Figure 3. Variation of pore volume of the ion-exchange resin versus polymerization time for 20% DVB.

more than the one for ion-exchange resins. This indicates that polysiloxane is a suitable substrate for the catalyst coating.

Catalytic, physical and chemical properties of produced catalysts

The double coated packings were used as catalyst in production of methyl tertiarybutylether, MTBE. The most important parameters of catalysts are their catalytic properties. In this study, pore volume, effective surface area, and acidic capacity were measured as other effective parameters the produced catalyst. Furthermore, the strength of the bonds between the aluminum-silica-gel and the ion-exchange resin was measured in the presence of water at a temperature of 25 °C and for a period of 3 days. The percent of swelling was calculated through usage of an electron microscope for measurement of film thicknesses. The calculation is based on the difference of film thicknesses before and after placing the samples in water. Table 2 presents the values of these properties.

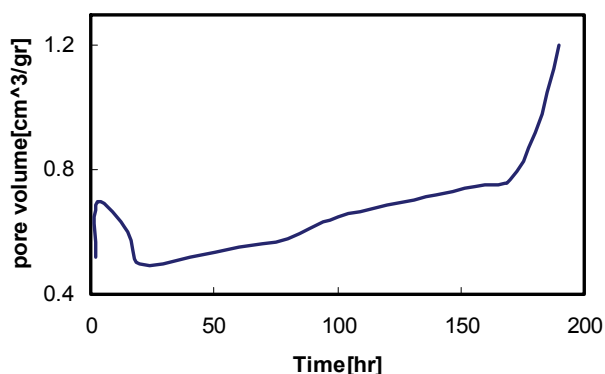


Figure 4. Variation of pore volume of the produced gel with time.

Table 2. Catalytic, physical, and chemical properties of coated aluminum with ion exchange resin

Experiment type	Units	Packing without coupling agent	Packing with a coupling agent
Acidic capacity (based on the resin weight)	(meq H ⁺)/g	3.20	2.70
Pore volume	cm ³ /g	0.11	0.23
Surface area	m ² /g	35.60	215.80
Unnotch izod	lb.ft/in	2.20	2.60
Swelling	%	72	8

CONCLUSION

The results of this research work have shown that coated packings with coupling agents (adhesion

promoters) have reasonable catalytic, chemical, and physical properties. This study was performed on production of a catalyst, but it may be used for various chemical systems. Swelling of catalyst and its separation from the surface of metal under various operational conditions was reported as the main problem. For prevention of those occurrences, the results of this project offer the following approach: increasing the percentage of divinylbenzene during the resin's production process and applying adhesion promoters based on the sol-gel process. In the specified ethyl silicate hydrolysis process, the rate of reaction was relative to the concentration of consumed acid. By increasing the concentration of used acid, the gel was formed at a faster rate. The sol was formed at pH 2. However, for formation of gel, the pH should be 8 to have equilibrium between H⁺ and OH⁻. The hydrolysis process was intensified in the presence of H⁺, while in the presence of OH⁻ the process of condensation polymerization was enhanced. For reduction of the gel formation time, the ratio of the initial concentration of water to the initial concentration of ethyl silicate should be set to a value of 8.

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NAUČNI RAD

NANOŠENJE KATALIZATORA NA BAZI POLIMERA NA METALNE POVRŠINE

Ovaj rad prikazuje rezultate proučavanja nanošenja katalizatora na bazi polimera na metalnu površinu. Stabilnost premaza na metalnim površinama je glavna karakteristika. Za sintezu adhezionih promotera na bazi mešavina polisilana koji se ponašaju kao posrednici korišćena je sol-gel tehnologija. Intermedijerni sloj je presvučen sintetisanim sulfonovanim polistiren-divinilbenzenom kao katalizatorom za produkciju MTBE u katalizovanom destilacionom procesu. Bubrenje katalizatora i njegovo odvajanje od metalne površine je poboljšano: i) povećanjem količine divinilbenzena u procesu proizvodnje smole i ii) primenom adhezionih promotera baziranih na sol-gel procesu. Brzina hidrolize etil silikata je intenzivirana povećanjem koncentracije korišćene kiseline, dok je polikondenzacija poboljšana prisustvom OH. Sol je formiran pri pH 2, dok je pogodna pH vrednost za formiranje gela iznosila 8. Pri odnosu početnih koncentracija vode i etil-silikata 8, vreme formiranja gel stanja je minimizirano.

Ključne reči: katalizator na bazi polimera; tehnologija površinskog presvlačenja; adhezioni promotori.