Alumina/silica aerogel with zinc chloride as an alkylation catalyst

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The alumina/silica with zinc chloride aerogel alkylation catalyst was obtained using a one step sol-gel synthesis, and subsequent drying with supercritical carbon dioxide. The aerogel catalyst activity was found to be higher compared to the corresponding xerogel catalyst, as a result of the higher aerogel surface area, total pore volume and favourable pore size distribution. Mixed Al–O–Si bonds were present in both gel catalyst types. Activation by thermal treatment in air was needed prior to catalytic alkylation, due to the presence of residual organic groups on the aerogel surface. The optimal activation temperature was found to be in the range 185–225 ºC, while higher temperatures resulted in the removal of zinc chloride from the surface of the aerogel catalyst with a consequential decrease in the catalytic activity. On varying the zinc chloride content, the catalytic activity of the aerogel catalyst exhibited a maximum. High zinc chloride contents decreased the catalytic activity of the aerogel catalyst as the result of the pores of the catalyst being plugged with this compound, and the separation of the alumina/silica support into Al-rich and Si-rich phases. The surface area, total pore volume, pore size distribution and zinc chloride content had a similar influence on the activity of the aerogel catalyst as was the case of xerogel catalyst and supported zinc chloride catalysts.

Keywords: aerogel catalyst, Friedel-Crafts alkylation catalyst, sol-gel derived catalyst.

INTRODUCTION

After dissolution of the reactants in an appropriate solvent and subsequent gelation of the sol, the wet gel formed can be dried by several methods. When elevated temperatures and atmospheric pressure or vacuum are applied, the obtained dry material is known as a xerogel. Another available drying method is the extraction of the solvent using supercritical drying, which preserves the original gel structure by eliminating capillary pressure. Solvent and sol-gel reaction byproducts present in the gel pores are extracted at a temperature and pressure higher than the solvent or the critical temperature and pressure of their mixture, or

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by another supercritical extracting fluid with moderate values of critical parameters (commonly carbon dioxide). Supercritical drying produces a material known as an aerogel.[1–3] Due to the unique properties of aerogels, they are being widely studied for potential applications in heterogeneous catalysis.[4]

Traditional Friedel-Crafts alkylation catalysts: HF, H_2SO_4, $AlCl_3$ or BF_3 dissolved in various solvents and acid treated clays have some serious disadvantages. These are: high corrosiveness, necessity to neutralize and separate the catalyst from the reaction mixture (in case of homogeneous catalytic systems), poor selectivity and difficult disposal of the spent catalyst. For these reasons supported metal halides, particularly zinc chloride, have been investigated as catalysts for Friedel-Crafts reactions in recent years. The most widely studied material, zinc chloride supported on Montmorillonite K10 (Clayzic), was first reported in 1989.[5] Since this 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 Clayzic is an effective catalyst.[6–9]

In this paper we present a one step sol-gel synthesis of alumina/silica gel with zinc chloride and its subsequent supercritical drying (solvent extraction with supercritical carbon dioxide), comparison of the aerogel and xerogel Friedel-Crafts alkylation acitivity, the aerogel catalyst optimal activation conditions and the determination of the optimal zinc chloride content of the aerogel catalyst. Catalyst samples were tested in the benzylation of benzene as a typical test reaction for Friedel-Crafts alkylation catalysts. The aerogel catalyst samples were characterized by thermomicroscopic analysis, thermogravimetric analysis coupled with FTIR spectroscopy, BET nitrogen adsorption, differential scanning calorimetry and FTIR spectroscopy. The products of the Friedel-Crafts reaction were analyzed using gas chromatography.

EXPERIMENTAL

Reagents

Anhydrous zinc chloride (Acros), 1-butanol (Merck), and tetraethoxy silane - TEOS, aluminium tri-*sec*-butoxide and benzyl chloride (all Fluka) were used as reagents.
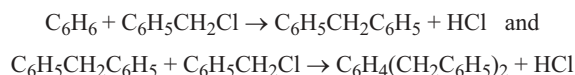
Catalyst preparation

Sol-gel-synthesis. The sol-gel synthesis was performed according to Miller *et al.*[10] Aluminium tri-*sec*-butoxide (9.84 g, 0.04 mol) was mixed with 1-butanol (100 cm^3) and then TEOS (8.32 g, 0.04 mol) was added. The mixture was stirred vigorously and heated at 70 ºC for 5 min until a clear solution was obtained. After cooling to room temperature, the solution was hydrolyzed with water (18.75 cm^3, 1.04 mol) in which zinc chloride (3.75 g, 0.025 mol) had already deen dissolved. The solution was stirred for 15 min and left to stand overnight (gelation). Water and some amount of the excess 1-butanol were then removed by heating to 150 ºC, whereby a "densed" wet gel was obtained. The above procedure describes a wet gel synthesis, with the quantities of reactants, solvent, water and zinc chloride found by Miller *et al.*[10] to be optimal for xerogel catalyst preparation.

Xerogel preparation. The "densed" wet gel sample was dried in an oven at 225 ºC (optimal drying temperature for xerogels as found by Miller *et al.*[10]) for 12 h.

Aerogels preparation. The "densed" wet gel sample, typically 12–14 g, was placed in a 70 cm^3 tubular extractor (Autoclave Engineers SCE Sreening System). The extractor was then filled with liquid carbon dioxide from a storage cylinder. To avoid two phases of carbon dioxide, the pressure

was first increased above the critical one (73.7 bar). Then, the temperature was raised (10 ºC/min) above the critical temperature of carbon dioxide (31.1 ºC), and maintained at the desired and fixed value. After reaching the desired extraction conditions, the carbon dioxide flow was started. In all supercritical drying (SCD) experiments, the flow rate was maintained at 90 g CO_2/h for 4 h. After this period, the flow was stopped and carbon dioxide removed from the tubular extractor at a temperature higher than the critical temperature of carbon dioxide (usually at a drying operation temperature in order to avoid the existence of two carbon dioxide phases). After that, the extractor was cooled down to room temperature and the sample removed from the extractor.

Catalyst testing procedure. Prior to activation, the catalyst samples were ground and sieved, and the fraction of 315–800 μm was used for each catalytic activity test. The catalyst samples were activated by heating in an oven at 185 ºC for 2 h prior to the catalyst activity tests. In a typical procedure, benzene was stirred with freshly activated catalyst. An aliquot of benzyl chloride was then added and the reaction mixture stirred for 15 min at room temperature. 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 diphenylmethane as the dominant product. The following reactions occur in the system:

$$C_6H_6 + C_6H_5CH_2Cl \rightarrow C_6H_5CH_2C_6H_5 + HCl \quad \text{and}$$

$$C_6H_5CH_2C_6H_5 + C_6H_5CH_2Cl \rightarrow C_6H_4(CH_2C_6H_5)_2 + HCl$$

The catalyst was removed from the reaction mixture by filtration and the reaction product analyzed by gas chromatography. The conversion of benzyl chloride (X_B, %) was defined as the total molar conversion of benzyl chloride to diphenylmethane and ortho-, meta- and para-isomers of dibenzylbenzene.

Analysis. Gas chromatographic analysis was carried out using a Varian 3400 gas chromatograph equipped with a J&W Scientific DB-5 fused silica capillary column and a FID detector linked to a Spectra Physics System I intergator. Quantitative analysis was performed using 1-decanol as an internal standard. The relative linear shrinkage of the catalyst samples were monitored by an E. Leitz thermomicroscope (temperature range: 25–1100 ºC), at a sample heating rate of 10 ºC/min. Thermogravimetric analysis coupled with FTIR spectroscopy of the gaseous species removed by heating was carried out using a Bomem TG/plus TGA-FTIR instrument, under a dynamic helium atmosphere at a heating rate of 10 ºC/min. Textural characterization of the catalyst samples was performed using a Qunatachrome Autosorb Automated Gas Sorption System. The BET surface area, overall pore volume and pore size distribution (calculated using the BJH method) of the catalyst samples were obtained from nitrogen adsorption-desorption at 77 K. Differential scanning calorimetry curves were recorded with a Shimadzu DSC 50 instrument, at a heating rate of 10 ºC/min (temperature range: 25–700 ºC) in nitrogen. FTIR spectra were obtained using an MB Bomem instrument in the wavenumber range from 400 to 4000 cm^{-1}. The samples were prepared by the KBr method at a ratio sample/KBr = 1/100.

RESULTS AND DISCUSSION

Xerogel and aerogel catalytic activity and structure. The sol-gel synthesis conditions, supercritical drying conditions, catalytic activity in the benzylation of benzene, surface area and overall pore volumes of the xerogel and aerogel catalysts are given in Table I.

As it can be seen from the total conversion of benzyl chloride, the aerogel catalyst was more active than the xerogel catalyst. The larger surface area and overall pore volume of the aerogel catalyst indicate that the two catalysts have different porous structures. The relative linear shrinkage (Fig. 1) confirms that the porous structure of the

aerogel catalyst is different from that of the xerogel catalyst. The shrinkage of both the xerogel and aerogel shows an abrupt rise in the 750–850 ºC temperature region due to sintering. This rise is much more pronounced in the case of the aerogel while its shrinkage up to this temperature is lower than that of the xerogel. This type of behaviour upon heating is typical for aerogels,[11] due to their higher porosity and smaller particle size compared to the corresponding xerogels.

TABLE I. Total conversion of benzyl chloride in the benzylation of benzene (X_B), surface area (S_a) and overall pore volumes (V_p) of the xerogel and aerogel catalyst.

Catalyst	*SCD T*/ºC	*SCD P*/bar	X_B/%	S_a/m^2/g	V_p/cm^3/g
Xerogel	–	–	46	117	0.895
Aerogel	225	100	53	139	0.950

Sol–gel synthesis conditions: mole ratio Al/Si = 1, mole ratio H_2O/(Al+Si) = 13, volume ratio H_2O/C_4H_9OH = 0.1875, mole ratio $ZnCl_2$/Al = 0.625, gelation overnight, and gel heated to 150 ºC ("densed" gel).
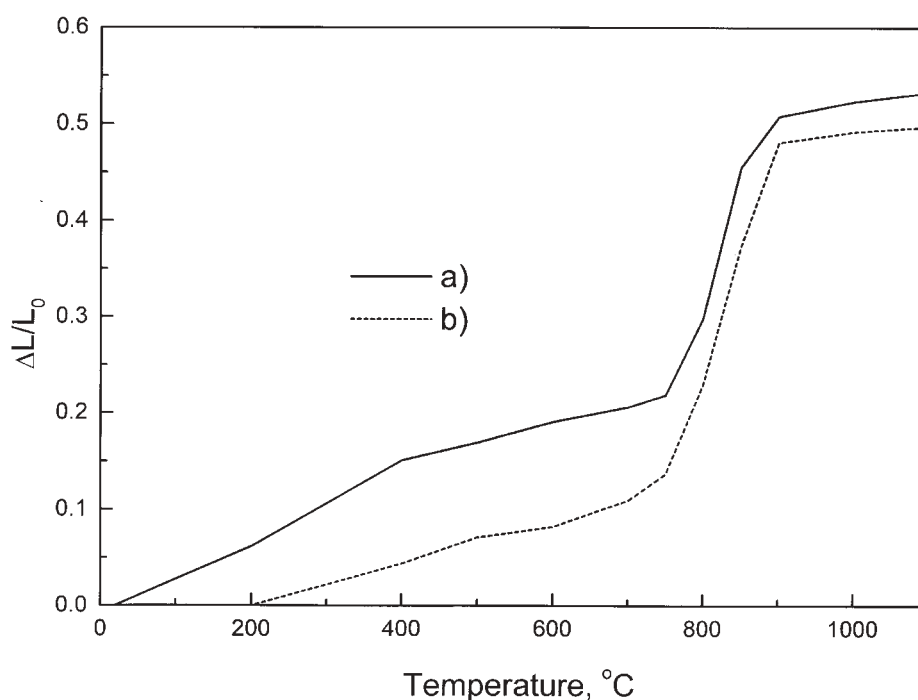

Fig. 1. Relative linear shrinkage plots of: a) xerogel catalyst and b) aerogel catalyst.

The pore size distribution plots of the xerogel and aerogel catalyst (Fig. 2) indicate that the distribution of the pore sizes is broad for both catalyst types. Rhodes and Brown[12,13] have investigated the influence of the pore size distribution of Clayzic (zinc chloride deposited on acid treated clay) and Silizic (zinc chloride deposited on silica) catalysts on the alkylation catalytic activity. Their results indicate that the optimal pore

radius is 5–6 nm. Pores with larger radius than the optimal are less active in the benzylation of benzene, while pores with pore radius smaller than the optimal are almost inactive. The surface area distribution of both catalyst types shows that pores with radii up to 4.8 nm constitute 52.8 % of the xerogel and 53.1 % of the aerogel surface area, pores with radii from 4.8 nm to 6.1 nm constitute 10.7 % of the xerogel and 12.4 % of the aerogel surface area and pore with radii above 6.1 nm constitute 36.5 % of the xerogel and 34.5 % of the aerogel surface area.
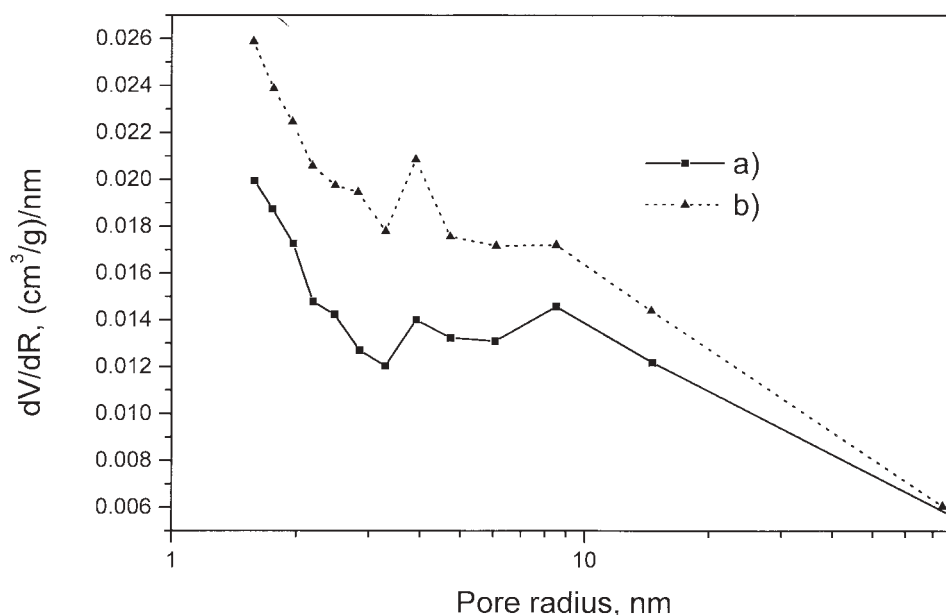

Fig. 2. Pore size distribution plots of: a) xerogel catalyst and b) aerogel catalyst.

The FTIR spectra of the xerogel and aerogel catalyst are shown in Figure 3. The band at about 1100 cm^{-1}, attributed to Si–O stretching vibrations,[14,15] shifts to lower wavenumbers: 1064 cm^{-1} for the xerogel and 1066 cm^{-1} for the aerogel catalyst. Other characteristic bands are: a band at about 460 cm^{-1} attributed to Si–O bending (present in the spectra of both the xerogel and the aerogel catalyst), a broad band 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.[14] The shift of the Si–O stretching vibration absorption band from 1100 cm^{-1} to lower wavenumbers indicates the presence of Al–O–Si bonds[14–16] in both gel types.

Since the alumina/silica structures of both catalyst types are very similar, the higher catalytic activity of the aerogel catalyst is explained by the larger surface area and overall pore volume, as well as the larger fraction of 4.8–6.1 nm radii pores.
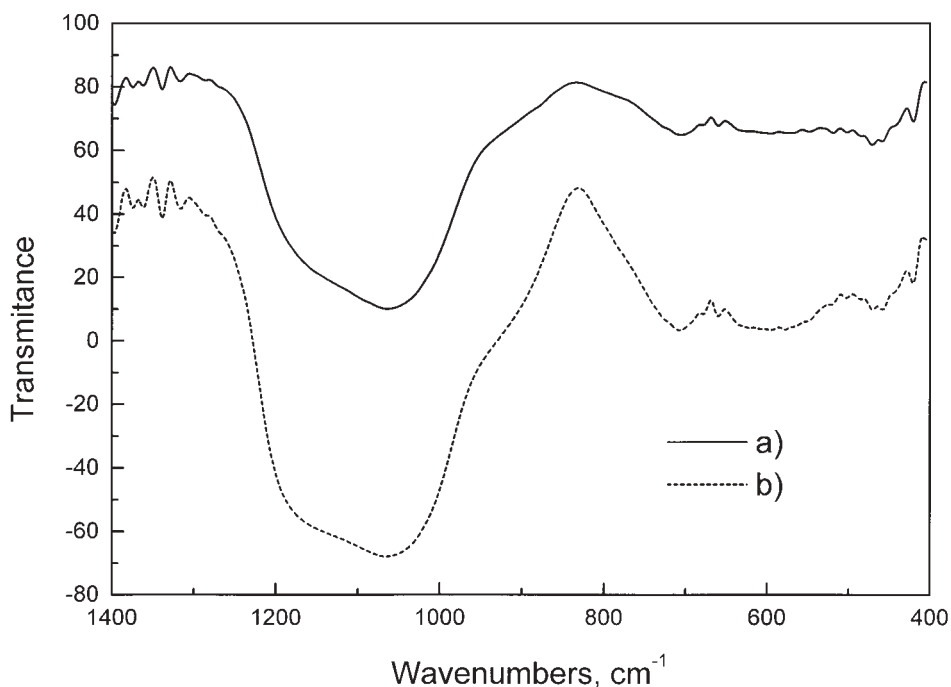
Fig. 3. FTIR spectra of: a) xerogel catalyst and b) aerogel catalyst.

Aerogel catalyst activation

The activation temperature of the aerogel catalyst influences the catalytic activity, as shown in Table II.

TABLE II. The influence of the aerogel catalyst activation temperature (catalyst samples were activated in air for 2 h) on the total conversion of benzyl chloride (X_B)

Activation $T/$ °C	130	185	225	275	335	510
X_B/%	26	57	57	47	46	6

The maximum catalytic activity of the aerogel catalyst is achieved after activation at 185–225 °C (Table II), while a dramatic decrease in the catalytic activity is observed after heating the catalyst to 510 °C. In order to elucidate the influence of the activation temperature on the catalytic activity, the aerogel catalyst sample was analysed using thermogravimetry (Fig. 4) coupled with FTIR spectroscopy of the released material. This method is unable to detect zinc chloride released from the catalyst surface, but provides information about the organic groups still remaining on the aerogel surface after supercritical drying.

The data presented in Fig. 5 show that adsorbed water is removed completely from the catalyst surface at 120 °C. Compounds containing CH_2 groups are released at temperatures between 36–184 °C. Carbonyl compounds are released in three temperature intervals: 50–178 °C, 252–372 °C and above 760 °C. CO_2 is released in two temper-
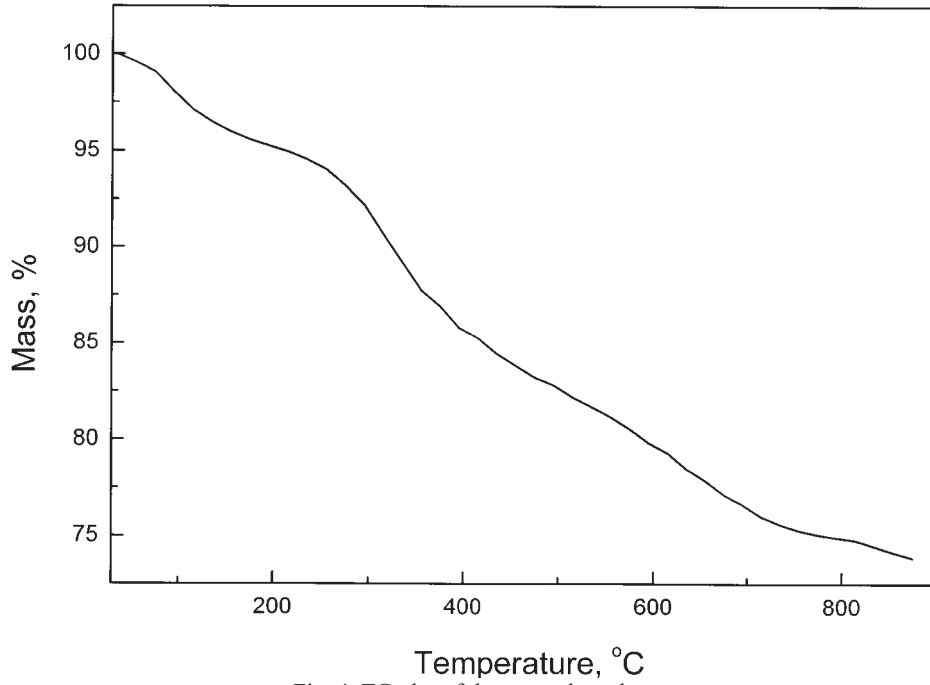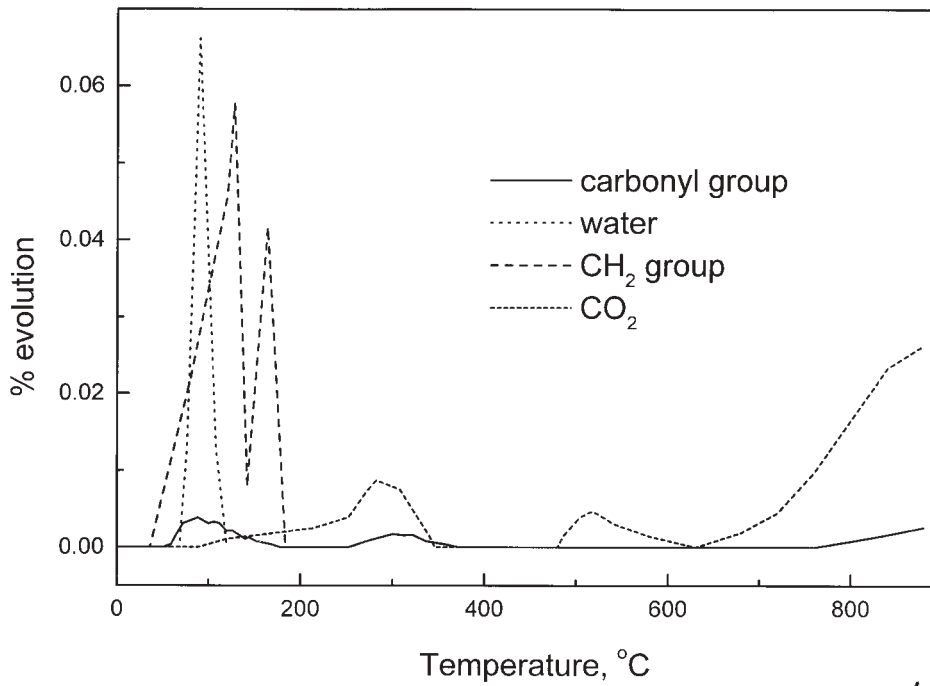
Fig. 4. TG plot of the aerogel catalyst.

Fig. 5. Evolution of the material released during heating of the aerogel catalyst.

ature intervals: 88–346 ºC and above 480 ºC. The presence of water on the catalyst surface is due to sample manipulation, while compounds containing alkyl groups, carbonyl compounds and CO_2 are the result of further condensation of terminal hydroxyl and alkoxy groups on the aerogel surface upon heating[1] and their subsequent thermal degradation. It is obvious that the maximum catalytic activity is obtained on the removal of not only water but also of compounds containing alkyl groups and carbonyl compounds from the aerogel surface. This indicates that residual alkoxy groups (remaining after supercritical drying) are blocking a certain fraction of the catalytically active surface. Further heating to 335 ºC results in the release of CO_2 and carbonyl compounds, and a certain decrease in activity. The aerogel catalyst loses its activity almost completely after heating to 510 ºC. The TGA plot (Fig. 4) indicates substantial weight loss from 200 ºC to 510 ºC (the total weight loss is 26.13 %), which is not evident from the released material evolution curves (total weight loss is 9.54 %). Zinc chloride leaching by washing the aerogel with water and analysing the filtrate by atomic absorption spectrometry showed that freshly dried aerogel catalyst contains 0.396 g $ZnCl_2$/g cat. while the sample heated to 510 ºC contains 0.231 g $ZnCl_2$/g cat. Evidently, heating the aerogel to 510 ºC results in the removal of zinc chloride from the aerogel surface, a reduction in the surface area and in the pore volume (Fig. 1) and a decrease in activity.[10]

Zinc chloride content

The conversion of benzyl chloride using aerogel catalysts with different zinc chloride contents is shown in Table III.

TABLE III. The influence of the zinc chloride content on the total conversion of benzyl chloride (X_B), sol–gel synthesis conditions, catalyst surface area (S_a) and overall pore volume (V_p) of the catalyst.

Catalyst	Mole ratio $ZnCl_2$/Al	X_B/%	S_a/m²/g	V_p/cm³/g
AG1 aerogel	0.3125	3	164	1.138
AG2 aerosol	0.625	53	139	0.950
AG3 aerogel	1.25	11	35	0.117

Sol–gel synthesis conditions: mole ratio Al/Si = 1, mole ratio H_2O/(Al+Si) = 13, volume ratio H_2O/C_4H_9OH = 0.1875, gelation overnight, gel heated to 150 ºC ("densed" gel), *SCD T* = 225 ºC, and *SCD P* = 100 bar.

On varying the zinc chloride content, the catalytic activity of the aerogel shows a maximum. In similar type of catalytic systems (supported zinc chloride), the active group is considered to be an isolated zinc chloride moiety supported on the framework, with a structure very different from crystalline zinc chloride.[12,13] The maximum catalytic activity is achieved when there is a monolayer surface coverage of zinc chloride and the mesopores are filled. Further addition of zinc chloride results in a system in which the zinc chloride is structurally more like crystalline zinc chloride. Since zinc chloride itself shows very little Friedel-Crafts activity, the observed catalytic activity decreases. It seems that in the case of the aerogel catalyst, the zinc chloride content has a similar influence on the catalytic activity. The catalyst with a low content of zinc chloride (AG1) is almost inactive due to insufficient surface coverage with zinc chloride. Increasing the zinc chloride content increases the catalytic activity (AG2) and reaches an
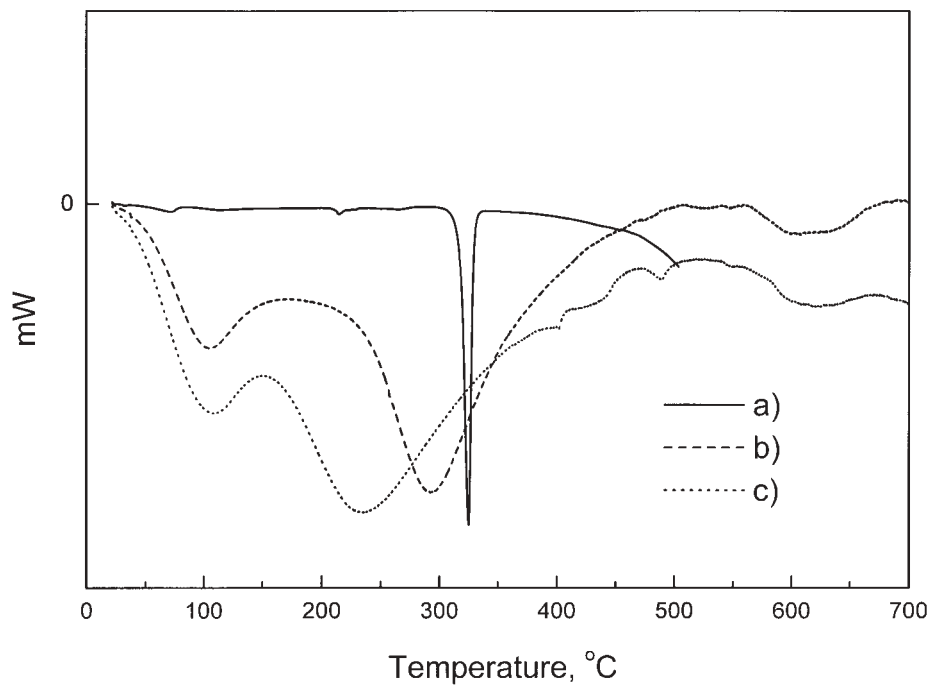
Fig. 6. DSC traces of: a) crystalline zinc chloride, b) aerogel catalyst AG2 and c) aerogel catalyst AG3.
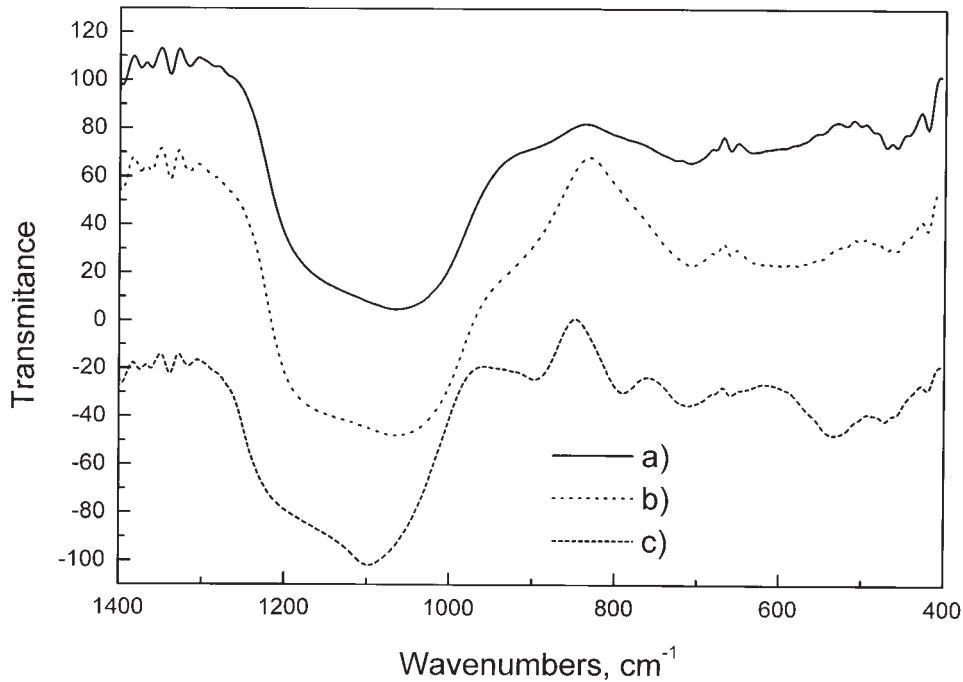

Fig. 7. FTIR spectra of: a) aerogel catalyst AG1, b) aerogel catalyst AG2 and c) aerogel catalyst AG3.

activity maximum, while further addition of zinc chloride (AG3) leads to a decrease in the catalytic activity. The specific surface area and overall pore volume decrease (AG3) confirm that the addition of zinc chloride leads to a filling up of the mesopores and a catalytic activity decline.

The structure of zinc chloride in the aerogel catalyst is different from that of crystalline zinc chloride, as confirmed by the broad endotherms around 300 ºC on the DSC traces (Fig. 6). A sharp endotherm of the melting of crystalline zinc chloride was not observed even for the very high zinc chloride content catalyst (AG3), indicating good dispersion of zinc chloride even in this case. Additional zinc chloride, on the other hand, influences the structure of the alumina/silica support.

The FTIR spectra presented in Figure 7 show that a high content of zinc chloride causes the separation of the alumina/silica aerogel network into Al-rich and Si-rich phase, and the disappearance of Al–O–Si bonding. The absorption bands for the catalyst with a high zinc chloride content (AG3) are: 1097 cm^{-1} (Si–O stretching), 470 cm^{-1} (Si–O bending), 534 cm^{-1} (octahedral Al–O), 712 cm^{-1} (tetrahedral Al–O), 800 cm^{-1} (octahedral Al–O or symmetric Si–O streching) and 890 cm^{-1} (tetrahedral Al–O). This indicates almost complete separation of the alumina/silica aerogel network into Al–O and Si–O phases. However, the FTIR spectra of catalysts with lower zinc chloride contents indicate the presence of Al–O–Si bonds in their structure (AG1 and AG2).

CONCLUSION

Alumina/silica aerogels with zinc chloride were obtained by a one step sol-gel synthesis followed by supercritical drying using supercritical carbon dioxide. The catalytic activities of the produced aerogel alkylation catalysts were found to be superior to the corresponding xerogel catalysts. The reasons for the higher catalytic activity of the aerogel catalysts are: larger surface area, larger overall pore volume and favourable pore size distribution. Residual organic groups are present on the aerogel surface after supercritical drying. Subsequent heating of the aerogel to 185–225 ºC is needed, in order to remove residual surface organic groups and achieve maximum catalytic activity. Further heating of the aerogel catalyst leads to the removal of zinc chloride from the aerogel surface and activity loss. On varying the zinc chloride content, the catalytic activity of the aerogel catalyst shows a maximum. This is in accordance with the results previously published for zinc chloride deposited on acid treated clay and silica, and xerogel catalyst. Higher contents of zinc chloride result in the filling up of the aerogel pores, separation of the alumina/silica support into Al-rich and Si-rich phases, and lower catalytic activity. The pore size distribution and zinc chloride content have a similar influence on the catalytic activity of the aerogel catalyst, xerogel catalyst and catalyst with supported zinc chloride, indicating the same catalytic mechanism of these catalysts.

ALKYLATION CATALYST 695

И З В О Д

АЛУМОСИЛИКАТНИ АЕРОГЕЛ СА ЦИНК-ХЛОРИДОМ КАО КАТАЛИЗАТОР ЗА РЕАКЦИЈЕ АЛКИЛОВАЊА

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Алумосиликатни аерогел са цинк-хлоридом као катализатор за реакције алкиловања, добијен је једностепеним сол-гел поступком и накнадним сушењем са наткритичним уг-љен-диоксидом. Утврђено је да је каталитичка активност аерогел – катализатора виша од каталитичке активности одговарајућег ксерогел – катализатора, због веће специфичне по-вршине и укупне запремина пора аерогел – катализатора, као и повољније расподеле ве-личина пора. Оба типа гел – катализатора поседују мешовите Al–O–Si везе у структури алумосиликатног носача. Због присуства заосталих органских група на површини аерогел катализатора, пре каталитичког алкиловања неопходна је активација катализатора загре-вањем на повишеној температури у атмосфери ваздуха. Оптимална температура активације је у опсегу 185–225 ºC, док је виша температура активације резултирала уклањењем цинк-хлорида са површине катализатора и значајним смањењем каталитичке активности. Зависност каталитичке активности од садржаја цинк-хлорида је показала максимум. Високи садржај цинк-хлорида је довео до пада каталитичке активности услед запуњавања пора катализатора овим једињењем и сепарације алумосиликатног носача на фазе богате алу-минијумом и силицијумом. Утврђено је да специфична површина, укупна запремина пора, расподела величина пора и садржај цинк-хлорида, имају сличан утицај на активност ае-рогел-катализатора као и на активност ксерогел-катализатора и катализатора добијених наношењем цинк-хлорида на различите носаче.

(Примљено 5. априла 2001)

REFERENCES

1. C. J. Brinker, G. W. Scherer, *Sol–gel Science*, Academic Press, Boston 1990
2. J. Fricke, A Emmerling, *J. Amer. Ceram. Soc.* **75** (1992) 2027
3. D. W. Matson, R. D. Smith, *J. Amer. Ceram. Soc.* **72** (1989) 871
4. D. A. Ward, E. I. Ko, *Ind. Eng. Chem. Res.* **34** (1995) 421
5. J. H. Clark, A. P. Kybett, D. J. Macquarrie, S. J. Barlow, P. Landon, *J. Chem. Soc. Chem. Commun.* (1989) 1353
6. J. H. Clark, S. R. Cullen, S. J. Barlow, T. W. Bastock, *J. Chem. Soc. Perkin Trans.* 2 (1994) 1117
7. S. J. Barlow, T. W. Bastock, J. H. Clark, S. R. Cullen, *Tetrahedron Lett.* **34** (1995) 3339
8. D. R. Brown, H. G. M. Edwards, D. W. Farwell, J. Massam, *J. Chem. Soc. Faraday Trans.* **92** (1996) 1027
9. J. Massam, D. R. Brown, *Catal. Lett.* **35** (1995) 335
10. J. M. Miller, D. Wails, J. S. Hartman, J. L. Belelie, *J. Chem. Soc. Faraday Trans.* **93** (1997) 2439
11. Dj. Janaćković, A. Orlović, D. Skala, S. Drmanić, Lj. Kostić-Gvozdenović, V. Jokanović, D. Uskoković, *NanoStructured Mater.* **12** (1999) 147
12. C. N. Rhodes, D. R. Brown, *J. Chem. Soc. Faraday Trans.* **88** (1992) 2269
13. C. N. Rhodes, D. R. Brown, *J. Chem. Soc. Faraday Trans.* **89** (1993) 1387
14. P. Colomban, *J. Mater. Sci.* **24** (1989) 3011
15. M. Ocana, V. Fornes, C. J. Serna, *Ceram. Inter.* **18** (1992) 99
16. M. Ocana, J. Sanz, T. Gonzales-Carreno, C. J. Serna, *J. Amer. Ceram. Soc.* **76** (1993) 2081