

## Aroma Retention in Sol–Gel-Made Silica Particles

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The retention performance of aroma molecules from different chemical classes (e.g., alcohols, esters, aldehydes, and terpenes) by silica particles made by hydrolysis of tetraethyl orthosilicate is investigated. Since particle morphology, porosity, and pore size distribution can be controlled by the sol–gel preparation method, the influence of the nanoconfinement in the microporous matrix on aroma retention is studied as well as the effect of the initial aroma load of the particles. As the porosity is decreased, aroma molecules are entrapped more efficiently in the silica particles. The retention performance decreased from alcohols > aldehydes ≥ esters > terpenes as with polar organic matrices. Open sol–gel-made silica particles show an increased retention with increasing aroma load, while denser silica matrices show a maximum retention with increasing load.

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**KEYWORDS:** Sol–gel encapsulation; silica; aroma retention

## INTRODUCTION

Porous sol–gel-made particles are used as encapsulation matrices for controlled release in the food and pharmaceutical industry. Of special interest in this study are matrices for encapsulation of nutraceuticals, flavors, and fragrances for the aromatization of food, cosmetics, packaging materials, or textile fibers (1). Sol–gel-made silica particles differ significantly from organic carriers due to their inorganic, inert, and thus biocompatible nature (2). The incorporation of organic molecules is a typical matrix encapsulation process, where the silica nanoparticles surround the molecules during the formation of the gel (3).

Enhanced retention and oxidative protection of aroma compounds was observed in plating experiments by Bolton and Reineccius (4) when using fumed silica rather than conventional organic aroma encapsulation matrices. Although the exact protection mechanism of silica is uncertain, it is believed to be a result of electrostatic interaction (such as hydrogen bonding between the aroma molecules and silica), physical protection from oxygen within the active sites, and uptake of singlet oxygen by silica. Furthermore, Zeller et al. (5) highlighted the potential of microporous materials such as porous carbohydrates as effective adsorbent aroma carriers. As a consequence, microporous sol–gel-made silicas are investigated here more closely as encapsulation matrices for various aroma compounds.

A basic introduction into traditional encapsulation techniques for aroma molecules is given by Risch and Reineccius (6) and

by Shahidi and Han (7). In general, two concepts of aroma retention are discussed: selective diffusion in glassy matrices (8) and entrapment in the so-called microregions (9). In conventional carrier systems such as maltodextrin-based materials, the glass transition of the material affects aroma retention. The objective is to entrap the aroma in a glassy matrix that inhibits its molecular mobility. Once in the glassy state, amorphous carriers exhibit very low permeation rates and the amount of released aroma depends on the chemical composition of the matrix, the pore and particle size, the size of the aroma reservoir pockets (microregions) entrapped within the particles, and the wall thickness around these areas. Smaller water molecules will be able to diffuse selectively, whereas the bigger, more volatile organic molecules are retained preferentially. In the concept of entrapment within microregions, the aroma molecules are associated with the carrier matrix and each other by hydrogen bonding to form complexes within these microregions (10). There, the influence of the physicochemical properties of volatiles and carbohydrate carrier is a decisive factor for aroma retention (11). The nature of the functional groups, molecular weight, polarity, and volatility of the aroma compound are key parameters in determining retention performance. Generally, the retention of high molecular weight molecules is favored. Molecular weight and size are linked, and smaller molecules diffuse more easily through the matrix during drying compared to bigger molecules. Retention seems to decrease with polarity (alcohols > ketones ≈ esters > acids) in different carbohydrate carriers (11). Boutboul et al. (12) observed the same retention pattern for different types of starches. However, exceptions to this indicate that other

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**Table 1.** Sol–Gel Solution Composition and Blank SiO<sub>2</sub> Powder Characterization for the Four Samples

	sol A	sol B	sol C	sol D
TEOS, mol %	8.7	8.7	2.4	2.4
ethanol, mol %	47.4	47.4	37.3	37.3
HCl, mol %	0.047	0.047	0.065	0.065
H <sub>2</sub> O, mol %	43.9	43.9	60.3	60.3
NaOH, M	0.9	0.09	0.9	0.09
$H = [H_2O]/[TEOS]$	5.1	5.1	25.3	25.3
pore volume, cm <sup>3</sup> /g	0.08	0.10	0.13	0.21
porosity, %	15.4	18.5	22.4	31.5
SSA, <sup>a</sup> m <sup>2</sup> /g	156.2	188.1	283.2	403.7

<sup>a</sup> SSA values are indicative since powders are microporous.

physicochemical parameters besides chemical functionality are relevant; e.g., polar molecules are retained less than nonpolar ones and compounds with a higher relative volatility are lost preferentially. Overall, the retention of volatiles depends therefore on their steric hindrance, polarity, functionality, and relative volatility aside from the nature of the carrier matrix (13). Reineccius and Coulter (14) investigated the influence of spray-drying operating conditions on retention performance, and the in-feed aroma concentration was identified as one of the major parameters. An increase in aroma load resulted in a decreased retention performance. Therefore, these physicochemical parameters and the influence of aroma load are also investigated here to study the retention performance of silica carriers in comparison to conventional organic matrices.

Typically, a flavor consists of several chemical compounds that result in the desired smell and taste. Upon entrapment, however, this flavor composition may change by differences in retention of the individual compounds. This change in flavor composition has to be accounted for prior to designing an appropriate encapsulation matrix. Therefore, this study focuses on the retention performance of typical aroma molecules such as alcohols, aldehydes, esters, and terpenes to unravel the mechanisms of entrapment in sol–gel-made silica particles and to compare their performance with conventional carriers. It extends our earlier work on single component (decanoic acid) retention in silica matrices (15). As a consequence, the retention of a homologous series within these chemical classes was investigated. Furthermore, the silica particle characteristics were controlled by the sol–gel preparation method (16). The effect of aroma molecule nanoconfinement on retention performance was studied as well as the effect of initial aroma load.

## EXPERIMENTAL PROCEDURES

**Materials and Synthesis.** Four standard protocols (Sol A–D) were used in this study for aroma encapsulation (Table 1). Typically, TEOS (tetraethyl orthosilicate, Sigma Aldrich, Germany, 98%), absolute ethanol (Baker, Switzerland), deionized H<sub>2</sub>O (18 MΩ·cm at 25 °C), and 0.06 M HCl (prepared from a 1 M stock solution; Merck KGaA, Germany) were mixed in a beaker at room temperature in the molar ratios given in Table 1. Hydrolysis was carried out for 48 h. To induce gelation, the sol was neutralized with either a 0.09 or a 0.9 M NaOH solution (prepared from a 1 M stock solution; Merck KGaA, Germany). At pH 6 the aroma mixture was added to the sol, and after neutralization, gelation took place. The obtained gel was dried in a vacuum oven at 40 °C and 750 mbar for 24 h. Blank and aroma-loaded particles were prepared accordingly.

Table 2 shows physicochemical properties of the investigated aroma molecules. The single aroma compounds were received from Fluka (Switzerland). For each chemical class (esters, aldehydes, alcohols, and terpenes) an artificial mixture with equal proportions of each component for every homologous series (e.g. alcohol) was prepared. For example

**Table 2.** Physicochemical Properties of the Aroma Molecules

aroma component	MW, g/mol	bp, °C	$K_{ow}$ <sup>a</sup>
butanol	74.12	117.7	0.88
octanol	130.23	195.1	3.00
decanol	158.29	231.1	4.57
ethyl butanoate	116.16	121.5	1.85
ethyl hexanoate	144.22	167	2.83
ethyl octanoate	172.27	208.5	3.81
ethyl decanoate	200.32	241.5	4.79
hexanal	100.16	131	1.78
octanal	128.22	171	2.78
decanal	156.27	208.5	3.76
myrcene	136.23	167.1	2.44
limonene	136.23	176	4.57
linalool	154.25	197	2.97

<sup>a</sup> Oil/water partition coefficient.

when alcohol was used as aroma, it contained one-third by weight of butanol, octanol, and decanol. The initial mass fraction  $x_{i0}$  for each aroma component  $i$  in the sol–gel matrix was determined by

$$x_{i0} = \frac{m_{i0}}{\sum_i m_{i0} + m_{S0}} \quad (1)$$

where  $m_{i0}$  is the input mass of each aroma component and  $m_{S0}$  the dry amount of silica, which was calculated by assuming complete hydrolysis of the precursor. The total initial aroma mass fraction  $x_{tot}$  is defined accordingly:

$$x_{tot} = \frac{\sum_i m_{i0}}{\sum_i m_{i0} + m_{S0}} \quad (2)$$

Aroma-laden silicas A–D were prepared with total initial mass fractions  $x_{tot}$  ranging from 5 to 50 wt %. The hydrophobic terpenes were scarcely soluble in the sol, and an emulsion was obtained for initial mass fractions exceeding 5 wt %. Therefore, a homogeneous encapsulation could not be realized for samples exceeding 5 wt %. Terpene loads exceeding 10 wt % were not realized due to an inhomogeneous aroma distribution in the sol and the arising gel structure.

**Characterization and Instrumentation.** The N<sub>2</sub>-sorption isotherms of the powder samples were obtained on a Micromeritics ASAP 2010 surface area and pore size analyzer (Micromeritics, Nocrass, GA) at –196 °C (liquid nitrogen). All samples were degassed at 200 °C and 0.003 mmHg prior to the measurement. The surface and pore characteristics were calculated using Micromeritics software. To avoid any influence by helium adsorption on the nitrogen adsorption isotherm, the free space was measured in a separate experiment (17). The specific surface area was determined by multipoint BET using adsorption data in the pressure range ( $p/p_0$ ) from 0.05 to 0.25. In the case of a type I isotherm, the pore volume and particle porosity can be calculated from the amount of gas adsorbed in the plateau region (18). Assuming the ideal gas law with a liquid N<sub>2</sub> density of 0.808 g/cm<sup>3</sup>, the pore volume  $V_0$  is (19)

$$V_0 = 1.547 \times 10^{-3} V_A \quad (3)$$

where  $V_A$  is the adsorbed gas volume in cm<sup>3</sup>/g STP. With a silica density  $\rho_p$  of 2.2 g/cm<sup>3</sup> (2), the particle porosity  $\epsilon_p$  is (20)

$$\epsilon_p = \frac{V_0}{V_0 + 1/\rho_p} \quad (4)$$

Thermogravimetric measurements were carried out in a thermobalance (TGA/SDTA 851<sup>o</sup>, LF/1100 °C, Mettler Toledo AG). The silica powders (blank and aroma-laden) were initially heated in a pure oxygen flow (180 mL/min) from 30 to 1000 °C at a rate of 20 °C/min. In a second isothermal step, the powders were kept at 1000 °C for 15 min (21).

The aroma load was determined by extraction and subsequent GC analysis. Aroma-laden silica powder ( $m_E = 0.2\text{--}0.5$  g, depending on the aroma load), water (4 mL), and dichloromethane (20 mL) were mixed in 25 mL Pyrex bottles. Decanol was used as internal standard (0.1 mg/mL in dichloromethane). Extraction was carried out on extraction plates (Mettler Toledo, Switzerland) at a stirring speed of about 350 rpm for 24 h (although the extraction was already complete after 2 h). The plates were immersed in a temperature-controlled water bath ( $T = 15$  °C). In a subsequent step, the organic phase was taken and the residual water was removed with sodium sulfate before GC analysis.

The gas chromatograph (GC, Varian Chemstation 6890, Darmstadt, Germany) was equipped with a polar DB-FFAP column (J&W 123-3232, J&W Scientific, Folsom, CA) and a flame ionization detector (FID) at 250 °C. Helium was used as carrier (1.7 mL/min) and makeup gas (35 mL/min). The injection technique was on a column (40 °C) with a sample volume of 0.001 mL. The split injection mode was used at a 10:1 ratio. Initially the column was at 40 °C for 2 min, followed by a ramp of 4 °C/min up to 180 °C and then by another increase of 10 °C/min to the final 240 °C, where it was held for 10 min. The calibration was carried out with known concentrations of the corresponding pure aroma mixture (0.02–1.5 mg/mL in dichloromethane) with an internal standard of similar concentration. The calibration curves, consisting of at least five points, were linear ( $R^2 > 0.997$ ) for all aroma components shown in **Table 2**. The concentrations of each component were calculated according to the corresponding GC areas taking concentration and area of the internal standard into account. Each aroma-laden sample A–D was prepared twice as well as the corresponding blanks. Three extractions from each aroma-laden sample were carried out, and the extract was subjected to GC analysis four times. The same stock solution of internal standard was used throughout the study.

The change in pore structure upon encapsulation was obtained by heating the aroma-laden silica particles for 16 h in air in an oven (Carbolite, Sheffield, England) at 300 °C. At this temperature the silica structure remains unchanged. Most of the aroma and the degeneration products are removed from the pores, and the increase in pore size compared to the blank samples provides information about the size of the microregions created by the molecules during entrapment.

**Encapsulation of Aroma.** The total mass of sol-gel powder that is subjected to GC analysis ( $m_E$ ) consists of

$$m_E = m_{SE} + m_W + \sum_i m_i \quad (5)$$

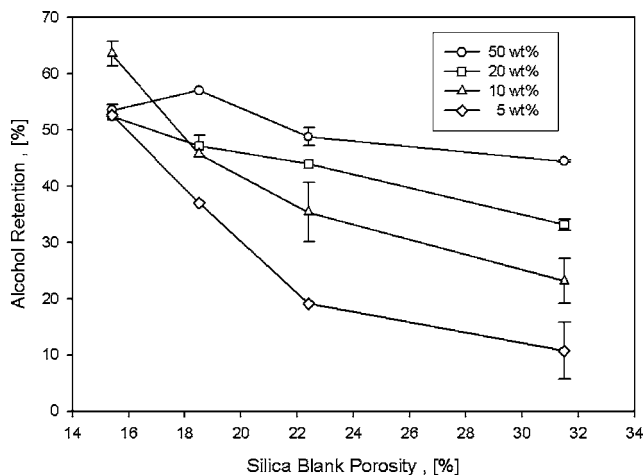
where  $m_i$  is the mass of the aroma component in the extraction sample determined by GC analysis,  $m_W$  the mass of water, and  $m_{SE}$  the mass of dry silica subjected to extraction, which is determined by thermogravimetric analysis (TGA) of the aroma-laden sample. The aroma retention  $R$  of each component  $i$  in the matrix is

$$R_i = \frac{m_i/m_{SE}}{m_{i0}/m_{S0}} \quad (6)$$

where the subscript 0 stands for the initial conditions. The weight loss of the aroma-laden sample,  $\Delta m$ , detected gravimetrically is given by

$$\Delta m = \sum_i m_i + m_W + m_{OH} \quad (7)$$

where  $m_{OH}$  is the mass loss attributed to thermal dehydroxylation of the silica surface. During dehydroxylation, a condensation reaction between two surface silanol groups ( $\equiv\text{Si-OH}$ ) results in one siloxane group ( $\equiv\text{Si-O-Si}\equiv$ ). Fully hydroxylated silica contains 4.6 OH/nm<sup>2</sup> (22–24). According to Vasant et al. (24), this value can be considered



**Figure 1.** Average alcohol retention (butanol, octanol, and decanol at equimolar initial composition) in silicas (**Table 1**) as a function of the blank porosity for total initial loads of 5, 10, 20, and 50 wt %.

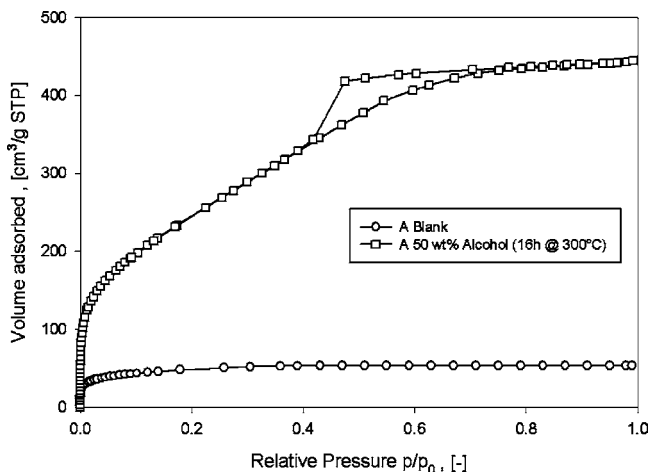
as a physical constant, regardless of the silica type and/or structure, e.g., pore size distribution or specific surface area. Thermal dehydroxylation leads to one residual OH/nm<sup>2</sup> at 800 °C and to 0.4 OH/nm<sup>2</sup> at 1000 °C (25). From the specific surface area (SSA) (**Table 1**) of the sol-gel-made powder and its change in OH-density during TGA, the contribution of thermal dehydroxylation,  $m_{OH}$ , to the total mass loss  $\Delta m$  can be quantified (21). Knowing the mass of all aroma compounds,  $m_i$ , from GC analysis, the mass of water in the sample can be determined by eq 7. Hence, the mass of the dry silica,  $m_{SE}$ , can be obtained by eq 5.

## RESULTS

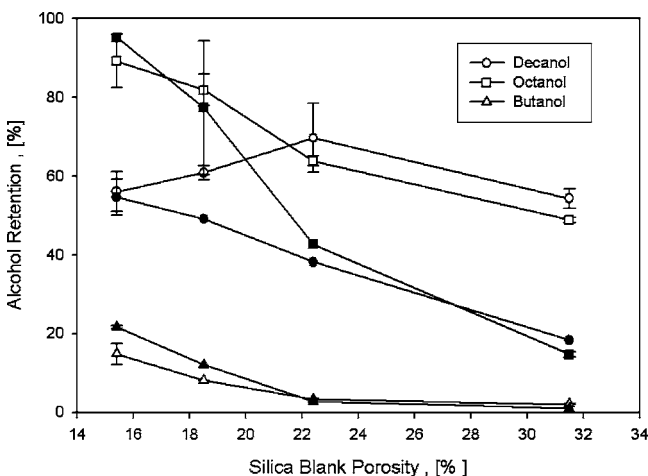
Sol-gel-made silica samples (with and without aroma) were prepared according to four different protocols (**Table 1**). The pore volume, porosity, and SSA of the SiO<sub>2</sub> powders A–D made without aroma are shown in **Table 1**. All isotherms exhibit type I behavior, which is characteristic for microporous solids, where the average pore size does not exceed 2 nm (17). Samples C and D, made at a high hydrolysis ratio ( $H = 25$ ), exhibit a higher specific pore volume and therefore a higher porosity compared to A and B, made at  $H = 5$  (**Table 1**), consistent with the work of Lenza and Vasconcelos (26) and Elferink et al. (27). The porosity increase is 45% (A to C) and 70% (B to D) (15).

### Aroma Retention and Influence of Particle Morphology.

(a) *Alcohols.* An aroma mixture containing butanol, octanol, and decanol in equal proportions was encapsulated in silicas (**Table 1**) with total initial aroma loads ranging from 5 to 50 wt %. **Figure 1** shows the average alcohol retention as a function of blank silica porosity for four different initial loads. The average retention increases with increased initial load and decreases with increasing porosity for all silicas. This is in contrast to conventional carbohydrate matrices, where aroma retention generally decreases as the load increases (14). Especially for lower initial loads, the retention is significantly increased with decreasing porosity as alcohol adsorption to the silica surface becomes more pronounced by an increased nanoconfinement in the pore space. For an initial load of 5 wt %, the retention is enhanced about 5-fold by halving the porosity. This trend, however, diminishes at higher loadings, indicating that the pore space could be too confined. **Figure 2** shows the nitrogen adsorption isotherm of the densest blank sample A and the corresponding aroma-loaded sample after removal of the alcohol. This sample was initially loaded with 50 wt % alcohol that was removed by heating the sample for 16 h at 300 °C. It can be seen that the pore volume increased



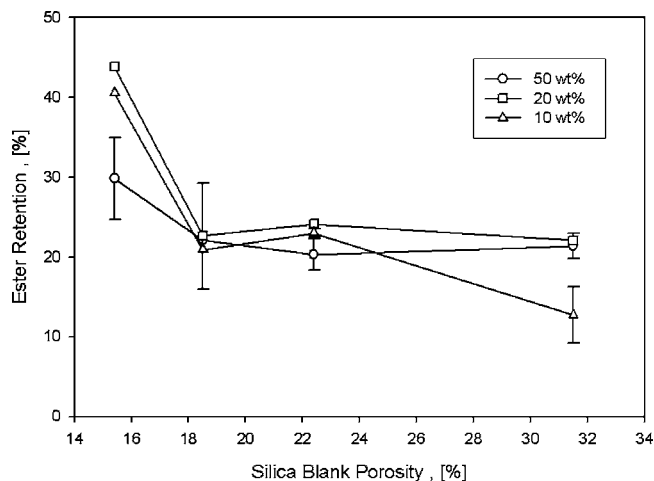
**Figure 2.** Nitrogen adsorption isotherms of the densest blank sample (circles, sample A in Table 1) and the corresponding one (squares) after removal of the alcohol by heating for 16 h at 300 °C. The latter sample was initially loaded with 50 wt % alcohol.



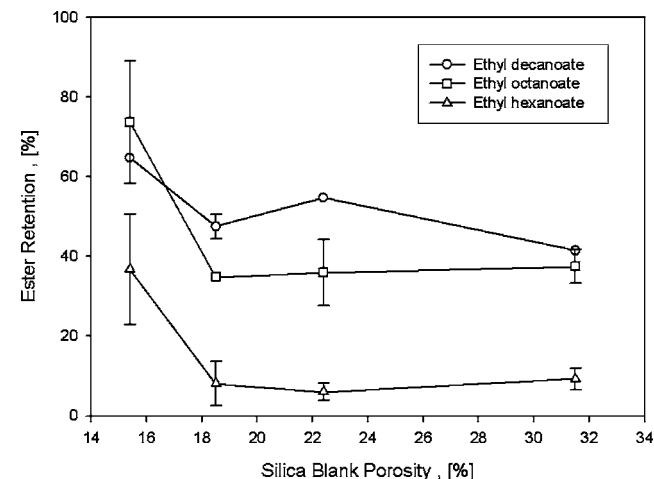
**Figure 3.** Individual alcohol retention in silicas (Table 1) as a function of the blank porosity for a total initial load of 20 wt % (open symbols) and 5 wt % (filled symbols).

drastically upon entrapment (28). During encapsulation aroma molecules seem to act as a template, over which silica polymer chains are forming. The total accessible pore space for encapsulation is therefore 0.70 cm<sup>3</sup>/g (eq 3), corresponding to a porosity of 62%. However, an initial alcohol load of 50 wt % would occupy about 1 cm<sup>3</sup>/g, assuming 100% retention. Hence, the available pore space is not sufficient to incorporate the total amount of aroma, and therefore, the retention is not affected by load anymore at lower porosities.

To compare the retention behavior of each alcohol, **Figure 3** shows their retention as a function of the blank silica porosity for an initial load of 20 wt % (open symbols). Smaller molecules such as butanol are retained rather poorly, whereas the bigger molecules, octanol and decanol, are retained far better. The increase in retention with reduced powder porosity can be seen for both butanol and octanol, while decanol deviates from this trend at low porosities. Possible reasons could be either that bigger molecules are less well entrapped, since they are squeezed out more easily during the gel shrinking process, or that they are no longer fully extracted from the denser particles. At lower initial loadings (5 wt %; filled symbols) this behavior is not that pronounced, since for all alcohols an increase in retention with decreased particle porosity can be observed. In general, a



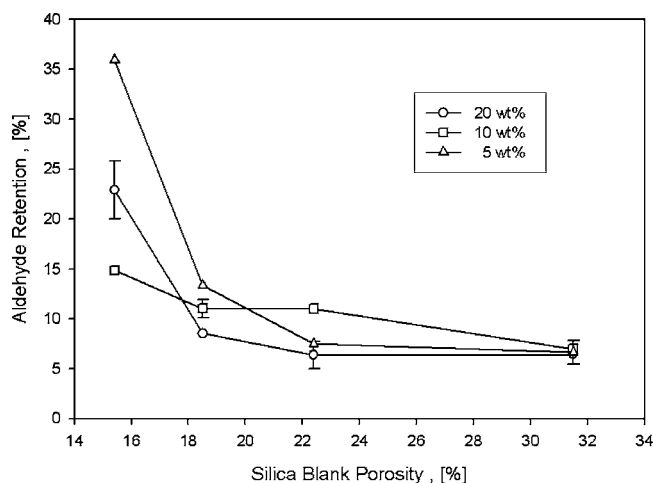
**Figure 4.** Average ester retention (ethyl butanoate, ethyl hexanoate, ethyl octanoate, and ethyl decanoate at equal initial weight proportions) in silicas (Table 1) as a function of the blank porosity for total initial aroma loadings of 10, 20, and 50 wt %.



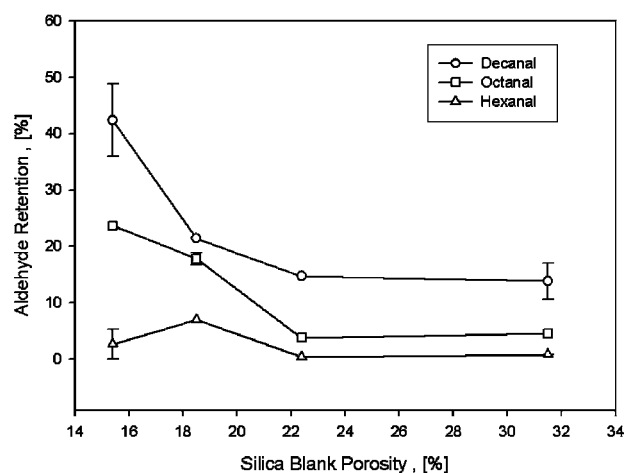
**Figure 5.** Individual ester retention in silicas (Table 1) as a function of the blank porosity for a total initial aroma load of 20 wt %.

decreased particle porosity and an increased aroma load lead to an enhanced alcohol retention. The retention pattern at a total initial load of 50 wt % (not shown) is similar to that at 20 wt %. The maximum alcohol content of the particles was up to 37 wt % (sample A, initial load 50 wt %), corresponding to an average retention of about 50%.

(b) *Esters.* In the ester series, an aroma mixture containing ethyl butanoate, ethyl hexanoate, ethyl octanoate, and ethyl decanoate (Tables 1 and 2) in equal weight proportions was entrapped in the sol-gel-made silica samples at total initial aroma loads of 10, 20, and 50 wt %. **Figure 4** shows that the average ester retention increases with decreasing blank silica porosity. Again, a drop in the total retention is observed at high loadings in the densest sample. **Figure 5** shows the retention of each ester component at an initial load of 20 wt %. Here again, the general trend is observed that, except for ethyl decanoate in the densest sample, bigger molecules with lower volatility (Table 2) are retained preferentially and that denser pore structures drastically increase the retention performance. This is also seen in samples with total initial loads of 10 and 50 wt % (not shown). However, small molecules such as ethyl butanoate could only be recovered to a small extent in the densest sample. The maximum ester load of 20 wt % was reached in the densest sample with an initial load of 50 wt %.



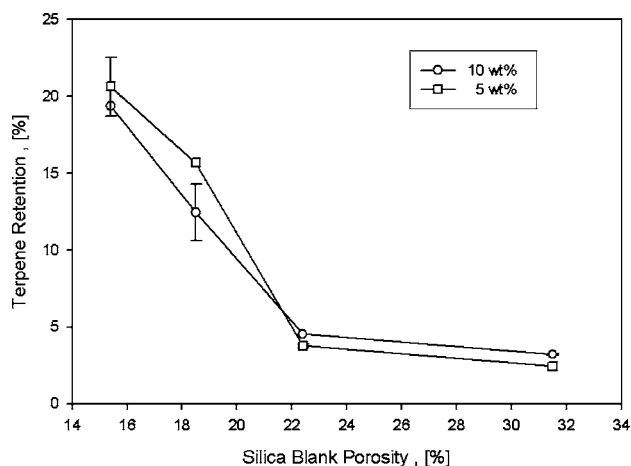
**Figure 6.** Average aldehyde retention (hexanal, octanal, and decanal at equal initial weight proportions) in silicas (Table 1) as a function of the blank porosity for total initial aroma loadings of 5, 10, and 20 wt %.



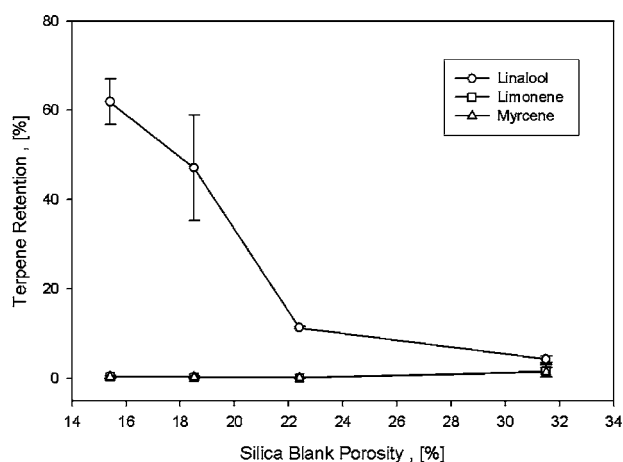
**Figure 7.** Individual aldehyde retention in silicas (Table 1) as a function of the blank porosity for a total initial load of 20 wt %.

(c) *Aldehydes.* An equal proportion mixture of aldehydes (hexanal, octanal, and decanal) was entrapped in sol-gel-made silicas at initial loadings of 5, 10, and 20 wt %. In sols with a higher aldehyde content, the aroma molecules were not soluble anymore. **Figure 6** also shows that the average aldehyde retention increases with decreasing blank porosity, especially in the sample with an initial load of 5 wt %. **Figure 7** shows the retention behavior of each aldehyde component at an initial load of 20 wt %, which is similar to samples with an initial load of 5 and 10 wt %. For all three components, a decreased blank porosity results in an increased retention. Large molecules of low volatility (Table 2) are retained better than smaller ones, as the former stay preferentially in the matrix during drying. Furthermore, bigger molecules possess lower diffusion coefficients that retard diffusional losses during drying. A maximum aldehyde load of about 5 wt % was reached in the densest sample with an initial load of 20 wt %.

(d) *Monoterpenes:* Terpenes [myrcene (methylene-7-methyl-1,6-octadiene), limonene (1-methyl-4-(1-methylethenyl)cyclohexene), and linalool (3,7-dimethyl-1,6-octadien-3-ol)] were entrapped in the sol-gel-made silicas (Table 1) of various blank porosities at total initial flavor loadings of 5 and 10 wt %. Terpenes are hydrophobic molecules, especially myrcene and limonene, that do not possess any polar groups. Hence, an emulsion was obtained in the case of an initial aroma load of



**Figure 8.** Average terpene retention (myrcene, limonene, and linalool at equal initial weight proportions) in silicas (Table 1) as a function of the blank particle porosity for total initial aroma loadings of 5 and 10 wt %.

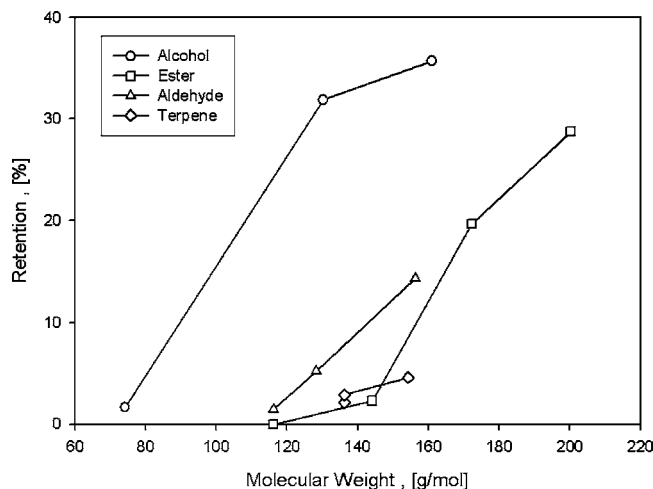


**Figure 9.** Individual terpene retention in silicas (Table 1) as a function of the blank particle porosity for a total initial load of 5 wt %.

10 wt %. In **Figure 8** the average retention of the terpenes in sol-gel silicas is shown as a function of the blank porosity. For all initial loads, the average retention can be increased with decreasing porosity. However, the average retention is only slightly increased with increasing aroma load in highly porous samples, whereas a decline in retention with increasing initial load can be noticed in the denser samples. But one should not forget that an emulsion was already obtained in the case of an initial aroma load of 10 wt %. The emulsion droplets are probably less well retained than single dissolved molecules, especially in low porosity samples. In **Figure 9** the retention of the single terpene components is presented. Myrcene and limonene as hydrophobic molecules are nearly not retained in contrast to linalool, which possesses a hydroxyl group that can interact with the hydrophilic silica surface. In the case of linalool, a decreased particle porosity increased its retention, in agreement with the other chemical series.

## DISCUSSION

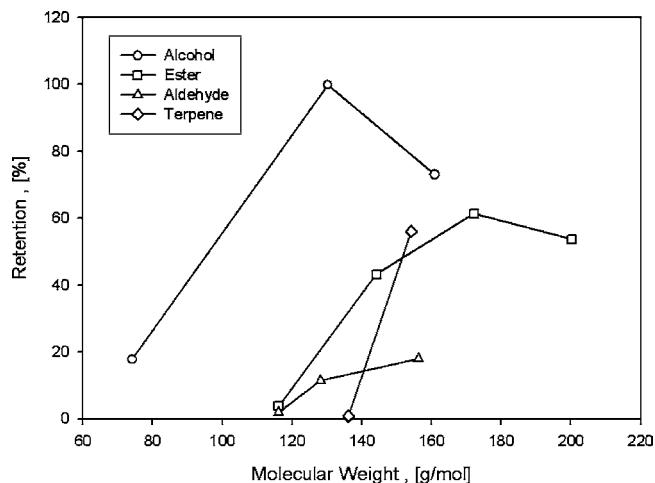
**Influence of Particle Morphology.** Retention of aroma components is a complex phenomenon in which several factors play a role. For sol-gel-made silicas the concept of entrapment in microregions seems to prevail. The above results show that aroma retention in porous silica sol-gel carriers can be influenced by the blank powder porosity and hence by the



**Figure 10.** Aroma retention in the most porous powder (sample D) as a function of the molecular weight of the employed species (Table 2) for a total initial load of 10 wt %.

hydrolysis ratio during their preparation (Table 1). As the porosity is decreased, the aroma molecules are believed to experience an additional nanoconfinement within the microporous network structure, resulting in an enhanced retention by capillary forces and a decreased diffusional loss during drying. Furthermore, the silica polymers in slowly hydrolyzing sol–gels (e.g., A and B) are still able to deform during drying, entrapping the aroma molecules more efficiently compared to more grainy, fast-hydrolyzing sols such as samples C and D made at high hydrolysis ratios (15, 28). In the microporous particles A and B an additional retention mechanism is therefore expected to take place. This is the nanoconfinement of the silica network applying a capillary pressure on the aroma molecules that increases the retention performance of the matrix as porosity is decreased. This was also observed by Smirnova et al. (29), who entrapped organic, pharmaceutical molecules in aerogels. The importance of the microstructure to improve aroma retention is furthermore discussed by Zeller et al. (5), Boutboul et al. (12), and Seuvre et al. (30). The presence of a functional group, however, that can either result in a chemical or physical interaction with the silica surface, seems to be a prerequisite for aroma retention. The terpenes myrcene and limonene are nearly not retained due to their hydrophobic nature, since they are not able to form any interactions with the hydrophilic silica surface. Boutboul et al. (12) investigated the influence and nature of different organic types of carrier materials (e.g. starches and maltodextrin). These hydrophilic materials show the same retention pattern as inorganic silicas. Molecules with an increased tendency to form hydrogen bonds with the starch matrix are retained preferentially.

**Influence of Chemical Nature.** The influence of the chemical class of the entrapped component is explored by comparing the sol–gel-made powders with the highest and lowest porosity. In Figure 10 a comparison of the retention performance of the different chemical classes in the most porous sample D is shown at an initial total load of 10 wt %. The retention of the homologous series is presented as a function of the molecular weight of the single components. It can be clearly seen that alcohols are retained better than any other compound with similar molecular mass. Alcohols are able to chemically react with the silica surface (31). In this chemisorption or condensation reaction the two hydroxyl groups of the silica and the alcohol react under separation of water to form a stable bond.



**Figure 11.** Aroma retention in the densest powder (sample A) as a function of the molecular weight of the employed species (Table 2) for a total initial load of 10 wt %.

Furthermore, hydrogen bonding between the hydroxyl groups can lead to a physisorption of the molecules on the silica surface (12, 32).

Esters and aldehydes both possess a carboxyl or carbonyl group, respectively, which provide similar interactions with the silica surface. They are both able to form hydrogen bonds with the silica surface, and hence, their retention performance is quite similar. However, aldehydes are also able to form hemiacetals with the silica surface, which may explain their slightly improved retention performance in comparison to the esters. The terpenes myrcene and limonene (same molecular weight) are nonpolar molecules that cannot form any interactions with the silica surface, resulting in a rather poor retention. Linalool (MW = 154 g/mol), however, possesses a hydroxyl group that can both chemically and physically adsorb to the silica surface, resulting in a better retention than the rest of the terpenes.

For alcohols, esters, and aldehydes, the retention performance is nearly linear with molecular weight. This is a general indication of physical adsorption between the molecules due to van der Waals forces, where every additional CH<sub>2</sub> group contributes to the energy of adsorption (33).

In Figure 11 the retention of the components of each chemical class is shown as a function of molecular weight for a total initial load of 10 wt % in the most dense silica matrix (sample A). The retention in the denser matrix (Figure 11) is better than in the more porous samples (Figure 10) for all species that can either chemically and/or physically adsorb to the silica surface. Furthermore, referring to the concept of encapsulation in microregions where molecules adsorb on the carrier surface and/or form associations among themselves, these regions are believed to be much more stable in a confined pore space (6). The influence of nanoconfinement can be nicely seen in the terpene series, where the retention performance of the nonpolar myrcene and limonene cannot be improved by a denser pore structure, in contrast to that of linalool, which increased from 4 to 50%.

A reduction in retention, however, is observed for the largest alcohol and ester molecules in the densest silica matrix. This can be either an indication that larger molecules are less well retained or that they cannot be fully extracted.

Conventional carbohydrate food carriers also offer hydroxyl groups to form hydrogen bonds with aroma molecules. A review about the physicochemical characteristics of both aroma and carrier and their influence on retention shows some interesting

parallels with the sol–gel-made materials (11). There it is stated that the functionality of the aroma molecules affects the retention performance. Moreover, the retention increases with molecular weight and decreases with the relative volatility of the aroma compound, in agreement with this study (34, 35). This behavior can be explained by the influence of the molecular weight on aroma diffusion through the matrix during drying. Diffusional losses decrease with increasing molecular weight. As a consequence, bigger aroma molecules will not be lost as readily compared to smaller molecules. However, a molecular size limit seems to exist for the sol–gel materials to be still able to release the aroma.

In general, comparing retention performances from Rosenberg et al. (34), Voilley (35), and Bangs and Reineccius (36) in carbohydrates as a function of the chemical nature of the aroma, alcohols were retained best. The retention seemed to decrease with polarity (alcohols > esters > aldehydes). Also Boutboul et al. (12) found a similar retention pattern (alcohol > aldehyde > ester > terpene) when investigating different starch carriers.

Rosenberg et al. (34) and Voilley (35) found that the retention in a homologous series decreases with increasing polarity. In general, the oil–water partition coefficients (Table 2) bear information about the polarity of the molecule. As the chain length increases, the oil/water partition coefficient increases as well, indicating a reduced polarity. In accordance with this study, Rosenberg et al. (34) observed that the more polar ethyl butanoate was less well retained compared to ethyl hexanoate in the ester series. Polar volatiles are more soluble in water and thus are believed to diffuse through the porous matrix influenced also by the drag imposed by the water molecules.

The lack of any hydrophobic interactions of the aroma molecules with the hydrophilic silica matrix seems to be responsible for the poor retention of the nonpolar terpenes myrcene and limonene. An introduction of a polar group (linalool) increases the retention performance. Alternatively, it would be possible to incorporate hydrophobic molecules into the sol–gel matrix (37, 38), which might lead to an increased retention of hydrophobic aroma molecules due to van der Waals forces. However, the use of these functionalized particles is limited to the aromatization of packaging materials, since the resulting ormosils (organic modified silicates) are no longer food-grade.

In contrast to carbohydrate matrices, where generally an increased aroma load leads to a decreased retention (14), sol–gel matrices show a different behavior. Particles with a more open porosity tend to show an increase in retention with an increased total load. Denser matrices, however, reveal either an optimum or a reduced retention with increasing load.

Encapsulating an aroma mixture containing different molecular species in sol–gel-made silica particles results in a shift of the aroma profile of the entrapped components toward bigger molecules. The retention performance decreases from alcohols > aldehydes  $\geq$  esters > terpenes. The release of molecules that just physically interact with the silica surface seems to be a simple desorption process (e.g., reversible hydrogen bonds). In the case of chemical adsorption, these bonds are believed to be reversible as well. However, release studies of aroma molecules in sol–gel-made silica particles reveal that smaller molecules are released much faster compared to bigger molecules. Furthermore, the initial aroma load defining the size of the microregions seems to be affecting the release kinetics even more (28). Higher loadings result in bigger microregions and hence bigger pore structures, from which the aroma is lost much faster compared to smaller microregions at low loadings.

Consequently, aroma load and release kinetics are coupled, which seems to be a unique feature of the sol–gel materials. Therefore, both aspects (encapsulation performance and release kinetics) would have to be taken into account when designing an artificial flavor mixture for sol–gel encapsulation.

#### ABBREVIATIONS USED

$H$ , hydrolysis ratio ( $H = [\text{H}_2\text{O}]/[\text{precursor}]$ );  $m_E$ , total mass of powder subjected to extraction (mg);  $m_i$ , mass of compound  $i$  in extraction sample (GC analysis) (mg);  $m_{i0}$ , theoretical aroma input mass of compound  $i$  (mg);  $m_{S0}$ , mass of silica in sol (mg);  $m_{SE}$ , mass of dry silica (extraction sample) (mg);  $m_{OH}$ , mass loss due to thermal dehydroxylation (mg);  $m_W$ , mass of water (extraction sample) (mg);  $R_i$ , retention of aroma component  $i$  (%); SSA, specific surface area ( $\text{m}^2/\text{g}$ );  $V_A$ , adsorbed gas volume ( $\text{cm}^3/\text{g}$  STP);  $V_0$ , total pore volume ( $\text{cm}^3/\text{g}$ );  $x_{i0}$ , initial mass fraction of component  $i$ ;  $x_{tot}$ , total initial mass fraction;  $\epsilon_p$ , particle porosity;  $\Delta m$ , total mass loss of aroma sample (TGA) (mg);  $\rho_p$ , particle density ( $\text{g}/\text{cm}^3$ ).

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