

SYNTHESIS AND CHARACTERIZATION OF ORGANO-MODIFIED SILICA AEROGELS

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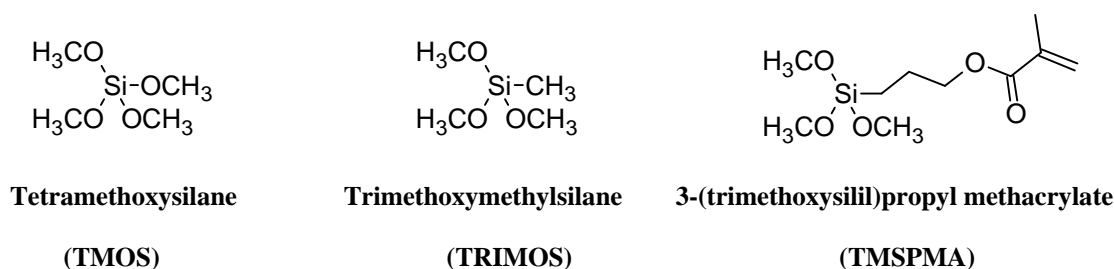
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Aerogels are extremely low density and highly porous solids (≥ 90 % of accessible mesoporosity), they can be synthesized by sol-gel methods and supercritical drying of the wet gels. In the case of silica aerogels, their extreme sensitivity to moisture and poor mechanical properties reduce its potentiality for technological applications. To overcome these shortcomings, a number of strategies have previously been investigated.¹ Here, we will report on two types of organo-modified silica gels resulting from condensing tetramethoxysilane (TMOS) with the organic groups trimethoxymethylsilane (TRIMOS) or 3-(trimethoxysilil)propyl methacrylate (TMSPMA) (Scheme 1). The concentration of organic part was increased until the gels lost their transparency (60 % TRIMOS; 25 % TMSPMA). The wet gels were dried either at supercritical conditions of methanol (high temperature drying) or by prior exchange of methanol with liquid CO₂ and subsequently drying the gels at supercritical conditions of the carbon dioxide (low temperature drying). FT-IR and solid-state ¹³C cross-polarity/magic-angle spinning (CP-MAS) NMR analysis confirmed that the high temperature drying causes degradation of the methacrylate chain, although the methacrylate is not affected by the low temperature drying.



Scheme 1. Molecular structures of alkoxides TMOS, TRIMOS and TMSPMA.

The materials with enhanced performance were those hybridized with TRIMOS and dried above the critical conditions of methanol.² For such series, we observed that when increasing the concentration of TRIMOS, the surface area increases and the average pore size diminishes. These hybrid aerogels were found to be hydrophobic, with a maximum contact angle over 160° for 60% of TRIMOS (Figure 1).



Figure 1. Piece of aerogel with 60% of TRIMOS with a water droplet on the top.

Solid-state ^{29}Si -NMR spectroscopy was used to determine the condensation degree and the number of superficial hydroxyl groups. Introducing TRIMOS into a TMOS system results in fewer condensations bonds and hence the degree of condensation decreases. We observed that the condensation degree radically decreases between TMOS:TRIMOS (100:0) and TMOS:TRIMOS (90:10). However, from 90:10 to 40:60, the degree of condensation remains almost constant even when the organic part is increased. According to this results, we can say that the difference in reactivity of TMOS and TRIMOS is not reflected in a regular decrease of the condensation degree.

Evaluating the number of superficial hydroxyl groups, we observed that as the organic part was increased, the contact angle increased and the percentage of $\equiv\text{Si-OH}$ bonds decreases. Such a decrease of $\equiv\text{Si-OH}$ bonds at the surface of the aerogel directly relates to the hydrophobicity of the material and is revealed by the increase of the contact angle. Our materials maintain the characteristic transparency of pure base catalysed silica aerogels for up to a molar ratio of 50% of TRIMOS. The materials absorbed more at shorter wavelengths and the absorbance increases as the amount of the organic part increases. Concerning the mechanical properties, they were measured using nanoindentation. We observed that as the organic part increases, the hybrid aerogel can be more easily deformed nevertheless the hardness is not affected. Table 1 gathers structural and mechanical properties of the TRIMOS series and reflects that the final properties of the material (contact angle, superficial hydroxyl groups, transparency, Young's modulus) can be tuned by controlling the degree of hybridation between the organic and the inorganic part.

Table 1.

	Contact angle (°)	$\equiv\text{Si-OH}$ (%)	Transmission (500 nm)	Young's modulus E (MPa)	Hardness H (MPa)
TMOS:TRIMOS (molar ratio)					
100 : 0	-	14.29	2.26	31.3	5.1
90 : 10	125	5.87	2.31	22.6	4.9
85 : 15	122	-	2.62	23.8	6.0
75 : 25	127	-	2.67	16.0	5.0
60 : 40	131	3.69	2.14	16.0	6.4
50 : 50	140	2.86	1.19	-	-
45 : 55	146	2.87	0.78	14.9	5.8
40 : 60	160	2.71	0.47	13.0	5.0

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