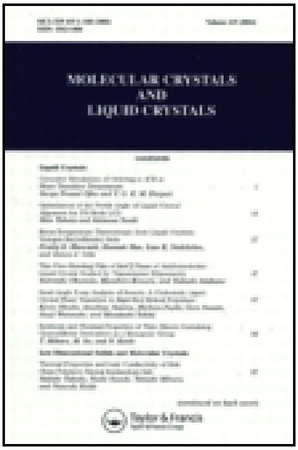

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Arylsulphonic Resins Based on Organic/Inorganic Macro-Molecular Systems

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ARYLSULPHONIC RESINS BASED ON ORGANIC/INORGANIC MACROMOLECULAR SYSTEMS

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Abstract Various organic derivatives of sepiolite, having $>$Si $CH_2CH_2C_6H_5$ groups which can be sulphonated, have been synthesized. The $-SO_3H$ functions introduced give the solid markedly acid character as shown by its ability to adsorb and protonate organic bases (pyridine), and in the catalytic dehydration of alcohols. The materials obtained have been identified by chemical analysis, IR and ^{13}C-NMR/MAS-CP spectroscopies.

INTRODUCTION

Various procedures have been described for the synthesis of cation-exchanger materials based on organosilicic compounds containing covalently linked aryl-sulphonic groups[1-6]. The basic idea consists of making improvements in some of the inherent properties of organic resins of poly-styrene sulphonic type, such as their thermal stability. In this way, starting from amorphous silica, materials have been prepared with $-C_6H_4SO_3H$ groups capable of taking part in catalytic procedures[3,7], chromatographic separation[5,8,9] and ionic exchange[2,4]. The published results on this theme are in some cases difficult to reproduce and the materials are not always rigorously described. The main difficulty in the synthesis of these products lies partly in the process of grafting of the aromatic groups on to the silica, partly in the control of the sulphonation of these groups.

EXPERIMENTAL

The starting material was sepiolite from Yunclillos, Toledo, Spain, which has been previously described[10], provided by TOLSA, S.A. The particle size was <200 mesh. This sepiolite is a hydrated magnesium silicate with microfibrous morphology, the half-cell formula being $Si_{12}O_{30}Mg_8(OH)_4(H_2O)_4 \cdot 8H_2O$[11]. Structurally (fig. 1) it is formed of blocks and channels extending in the fiber direction (c*-axis). Each structural block is made up of two tetrahedral silicic layers and a central octahedral layer containing magnesium.

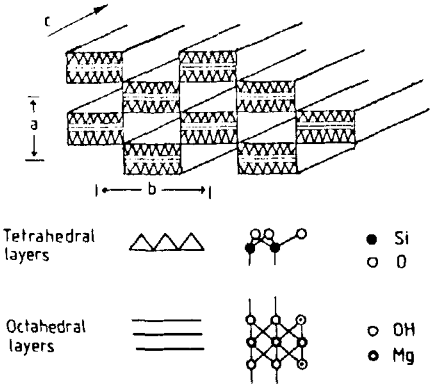


FIGURE 1. Schematic representation of a cross-section of a sepiolite fiber.

The synthesis of the arylsilicic derivate was carried out by co-hydrolysis[12] of the sepiolite (50.0 g) with 2-phenylethyl-methyl-dichlorosilane (I) (23.9 ml) in a mixture of HCl (37%) and isopropanol (250 ml/250 ml). The entire mixture was kept stirred continuously at 65°C for 9 h. The resulting solid was recovered by filtration, washed in a methanol/water mixture until no Cl^- ion was present, and dried at 110°C for 24 h. (compound II).

The sulphonation of compound II was carried out by treating the solid (5.0 g) dispersed in 10 ml of $CHCl_3$, with slow addition of 5 ml of $ClHSO_3$ keeping the mixture stirred at ambient temperature during 1 h. This mixture was poured on to a water/ice mixture (II), and the solid recovered by filtration and dialysis to constant pH ($\sim$3 days with constant renewal of the water). The aryl-sulphonic derivative (III) was finally removed by filtration and dried at 80°C for 24 h.

All the chemicals employed were Merck (analytical grade). The silane I was obtained from methyl-vinyl-dichlorosilane (Fluka, pract.) by Friedel-Crafts reaction with C_6H_6 in anhydrous $AlCl_3$.

The macromolecular ion exchanger Amberlist 15 (Rohm & Haas Co.) is a sulpho-polystyrene resin, strongly acid, with CEC = 480 meq/100 g. Specific surface area = 50 m^2/g. Particle size 16-50 mesh.

High resolution ^{13}C-NMR/MAS-CP spectra of the solids were recorded on the Bruker spectrometer CXP 400 MHz with a spinning frequency of 4-4.5 KHz. Accumulations: 1600 Fid's, Infrared spectra were recorded in the 4000-400 cm^{-1} region using a Perkin-Elmer 580 B double beam spectrophotometer coupled to an M-3500 data station, from self-consistent films.

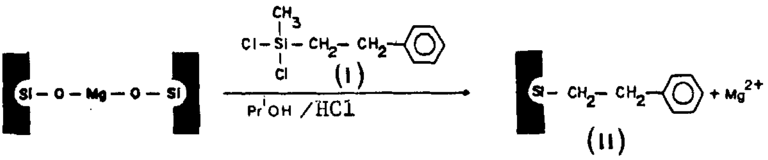
The adsoprtion of pyridine was carried out from solutions in n-heptane (5.10^{-3} N) and in the vapor phase (5 Torr). The vapor phase adsorption was carried out in an IR spectroscopic cell with CaF_2 windows, allowing for heating of the sample.

The catalytic tests were carried out in a pulse microreactor consisting of a Pyrex-modified gas-chromatography injector (Perkin-Elmer 8410; column 25 QC2 /CW 20M). Gas carrier: ultrapure dry N_2. Weight of catalyst: 10-20 mg. Range of temperature: $100\text{-}260 \pm 0.1$°C. Ethanol pulses: 0.1-0.5 µl.

RESULTS AND DISCUSSION

The process of obtaining the aryl-sulphonic derivative of sepiolite (compound III) occurs in two phases: i) synthesis of the arylsilicic derivative (II) by co-hydrolysis of sepiolite[12] with 2-phenylethyl-methyl-dichlorosilane (I) and ii) sulphonation of the II derivative by treatment with chlorosulfonic acid.

In the first phase (sheme 1) the Mg^{2+} ions in the



SCHEME 1. Grafting reaction of 2-phenylethyl-methyl-siloxyl groups on sepiolite (synthesis of arylsilicic compound II)

sepiolite are almost totally extracted (98%), with a recovery of 100 moles of $Si(CH_3)(CH_2-CH_2C_6H_5)$ groups from the residual silica, per 100 grams of solid (elemental analysis: 10.8 % C). XRD data show that the original ordered sepiolite structure disappears, although the microfibrous structure is largely preserved, as is observed by TEM. The specific surface area (BET, N_2) is 138 m^2/g; the diminution compared with the original sepiolite (340 m^2/g) is attributed to the blocking of micropores by the organosilane coating. The IR spectrum of derivative II shows the characteristic bands of the grafted groups: 3090, 3067 and 3031 cm^{-1} ($\nu_{CH} C_6H_5-$); 2966 ($\nu_{asym.CH}\ CH_3$); 2932 ($\nu_{asym}\ CH_3$); 1499, 1457 and 1412 cm^{-1} ($\nu_{CC}\ C_6H_5-$); 1263 ($\delta_{CH_3}\ -SiCH_3$) 754 and 701 cm^{-1} ($\gamma_{CH}\ C_6H_5$). The NMR spectrum clearly confirms the nature of the grafted organic groups (peaks at 0.41, 21.12, 31.18, 127.55, 130.10 and 146.80 ppm), shown in figure 2A.

The treatment of derivative II with chlorosulphonic acid (second stage:scheme 2) leads to the aryl-sulphonic compound III, whose elemental analysis (C: 13.0%; S:3.15%) indicates a 98 mmole content of $-C_6H_4SO_3H$ groups per 100 g. The specific surface area is 210 m^2/g, indicating that during the sulphonation some textural modification of the solid occurs. The IR spectrum is very similar to that of compound II, but there are further bands at 1375 cm^{-1} ($\nu_{asym}\ SO_2$) and 547 cm^{-1} (δ_{SO_2}), indicating the presence of sulphonic groups. The disappearance of the band at 754 cm^{-1} of the monosubstituted ring, and the appearance of a band at 785 cm^{-1} ($\gamma_{CH}\ -C_6H_4-$) shows that the substitution of the ring occurs in para position. There are no visible bands corresponding to trisubstituted rings,

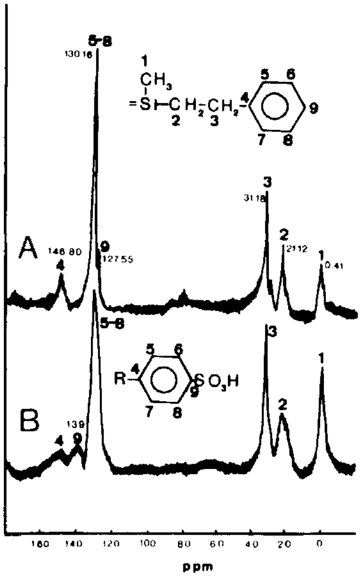
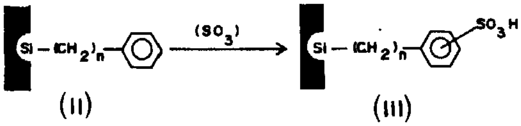


FIGURE 2. Spectra of ^{13}C-NMR/MAS-CP:
A) 2-phenylethyl derivative of sepiolite (Compound II)
B) Aryl-sulphonic derivative (compound III)



SCHEME 2. Sulphonation of the arylsilicic compound II (synthesis of the aryl-sulphonic derivative III; n=2).

which would correspond to disulphonic acids. This result is in agreement with the spectrum of ^{13}C-NMR (fig. 2B) in which the 127.55 ppm signal disappears (using C-atoms in para position), and the appearance of a new signal 139.0 ppm which may be assigned to the C-atom supporting the $-SO_3H$ group.

The activity conferred on the silicic substrate by the grafting of aryl-sulphonic groups is shown up by the ionic exchange properties, and the strongly acid character of the preparations obtained. In this sense, the adsorption of an organic base of the pyridine type (py) in an inert anhydrous solvent (n-heptane) is practically quantitative with respect to the $-C_6H_4SO_3H$ group content (80 mmoles of py/100 g; 98 mmoles of $-SO_3H$/100 g).

The adsorption of vapor phase py (5 Torr) was followed by IR spectroscopy on samples of derivative III previously subjected to thermal treatment (1h, 10^{-4} Torr) in the range 50-300°C. The bands observed at 1640, 1623, 1549 and 1493 cm^{-1} (fig. 3) are characteristic of the vibrations of the py-H^+ ion[14], which is formed with pretreatments of compound III near to 300°C according to the following scheme:

$$\underset{(III)}{-C_6H_4SO_3H} \quad + \quad \underset{(py)}{C_5H_5N} \longrightarrow \underset{(III\text{-}pyH^+)}{-C_6H_4SO_3\overset{+}{N}HC_5H_5}$$

The band at 1450 cm^{-1} is attributable to py adsorbed via hydrogen bonding[15]. Furthermore the band at 1380 cm^{-1} ($\nu_{asym}SO_2$) which is characteristic of the sulphonic group (and of pyridine sulphonate) is displaced to lower frequencies as a result of thermal treatment (elimination of H_2O molecules associated with $-SO_3H$) but its intensity does not diminish appreciably up to temperatures near 300°C, which is an indication of the good thermal stability of these aryl-sulphonic products.

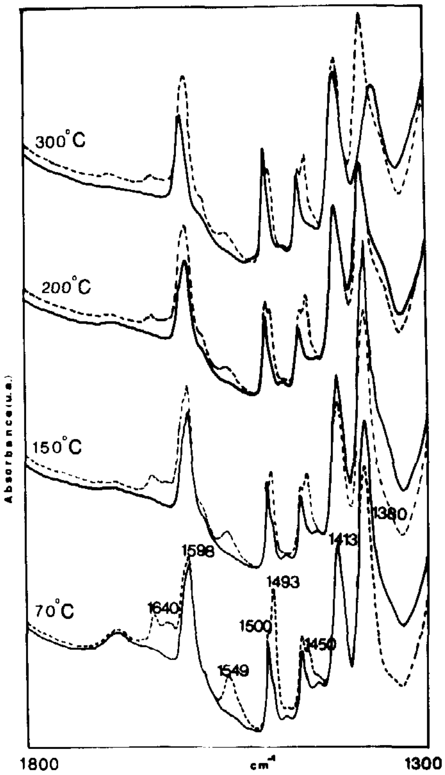


FIGURE 3. IR spectra in the 1800-1300 cm^{-1} region of the aryl-sulphonic derivative (compound III) treated thermally at various temperatures (——) and subsequently exposed to pyridine (---).

The highly acidic character and the thermal stability of these substances can be useful for their employment as active catalysts in proton-catalyzed reactions. With this in mind we carried out a series of trials of the dehydration of ethanol, chosen as a model molecule, using the aryl-sulphonic derivative III as catalyst. The rate of conversion with temperature (in the range of 100-260°C) was compared with that given by a commercial sulpho-polystyrene resin (Amberlist 15), which is often used as a highly acid catalyst in industrial processes[15-18]. The catalytic activity normalised for $-SO_3H$ content per unit weight is shown graphically in fig. 4. It can be seen that Amber-

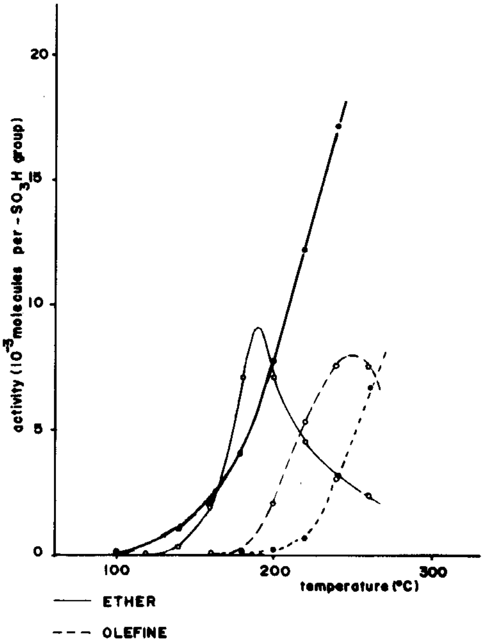


FIGURE 4. Catalytic activity vs temperature for ethanol dehydration to diethyl ether (——) and ethylene (---). ● Aryl-sulphonic derivative (compound III); o Amberlist 15.

list 15 shows a maximum in the conversion to ether around 190°C, while the catalytic activity of compound III increases greatly above this temperature. On the other hand the ethylene formation is less favorable with compound III than with Amberlist 15. The loss of activity of the Amberlist 15 resin is due to thermal decomposition which, according to various authors[6,19], takes place between 150-200°C.In this range we found,by gas chromatography,other unidentifiable products which may be due to fragmentation of the organic resin or to other by-products of the catalytic reaction. This does not occur with compound III.

CONCLUDING REMARKS

Our results show that the hybrid organo-mineral synthesized products posses functions due to SO_3H inserts in aromatic rings which, in their turn, are covalently attached to the mineral substrate. The highly acid character of these attached functional groups, together with their relatively high thermal stability, show potentially interesting uses for this type of material because of its properties of absorption and its surface reactivity.

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