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Synthesis and characterization of inorganic–organic hybrid materials based on the intercalation of stable organic radicals into a fluoromica clay

Ion exchange of fluoromica clay with nitroxide radical cations results in intercalation compounds that can serve as recyclable oxidation catalysts. The guest molecular orientation is composition dependent and controls the strength of intermolecular guest-host and guest-guest interactions.

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Introduction

Synthesis and characterization of inorganic–organic hybrid materials based on the intercalation of stable organic radicals into a fluoromica clay

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Hybrid materials, in which stable organic radical cations are intercalated into layered inorganic host materials, can be successfully synthesized via an ion exchange reaction in a layered fluoromica clay, to yield recyclable heterogeneous catalysts for oxidation of various alcohols. We have conducted systematic synthetic and structural studies on the intercalation of the radical cations 4-(diethylmethylammonium)-2,2,6,6-tetramethylpiperidin-1-oxyl (DEMTEP), 1-[2-(4-amino-2,2,6,6-tetramethyl-1-piperidinyloxyl)-2oxoethyl]-1'-methyl-4,4'-bipyridinium (VIOTEP), and 2-(3-N-methylpyridinium)-4,4,5,5-tetramethyl-4,5dihydro-1H-imidazol-1-oxyl-3-N-oxide (m-MPYNN) into a synthetic fluoromica clay named Somasif® ME 100, Na_{2x}Mg_{3.0-x}Si₄O₁₀(F_vOH_{1-v})₂ (x = 0.33, y = 0.98). The guest-host interactions in these intercalation compounds have been characterized by X-ray powder diffraction and solid-state NMR of the constituent nuclei (²³Na, ¹⁹F, and ²⁹Si) of the Somasif structure. The intercalation process can be conveniently monitored using ²³Na MAS-NMR. Guest-guest interactions have been probed by magnetic susceptibility measurements as well as EPR and ¹H MAS NMR experiments. The ¹H MAS-NMR line widths and chemical shifts probe modifications in the electron spin density distributions and/or intermolecular interactions between the electron spins of the quest species. Despite these indications of weakly interacting spins, magnetic susceptibility measurements are consistent with the near-absence of cooperative magnetism. The VIOTEP and DEMTEP inclusion compounds demonstrate catalytic activity for the oxidation of benzyl alcohol, using NaOCI as a co-oxidant. Although the radical ion species is partially leached out under these conditions (ionic exchange with Na⁺ in solution) the catalytic activity remains for up to 40 subsequent cycles. Fully leached materials can be regenerated by catalyst re-loading and this process can be conveniently monitored by X-band EPR spectroscopy.

Inorganic–organic hybrid materials involving stable organic radicals are a class of materials exhibiting a range of interesting and unusual optical, magnetic, and catalytic properties. Designing particular physical properties requires an understanding and synthetic control of the two basic intermolecular interaction types – on the one hand, those involving the host and the guest species, and on the other hand, those among the guest species themselves. For example, immobilization of the radical species on surfaces and/or self-assembly *via* hydrogen-bond interactions can lead to orientationally ordered electron spin arrangements, offering the prospect of cooperative magnetism.^{1,2} One particular type of hybrid material can be formed by intercalating the spin carrying molecule in the form of a radical cation into an inorganic layered host structure via an ion exchange reaction, whereby various possible orientation scenarios can be realized (Fig. 1). This principle has been demonstrated for some layered crystalline host matrices such as the clay material saponite Na_xMg₃Si_{4-x}Al_xO₁₀- $(OH)_2 \cdot nH_2O$ and cadmium phosphorus sulfide CdPS₃.³⁻⁷ As previously discussed, such materials can be used as recyclable catalysts for the oxidation of alcohols. In the present study, we report the intercalation of three different types of radical cations, based on tetramethylpyridine N-oxide (TEMPO), a nitronyl nitroxide, and a viologen into a fluoromica clay material known under the trade name Somasif, Na_{2x}Mg_{3.0-x}- $Si_4O_{10}(F_yOH_{1-y})_2$ (x = 0.33, y = 0.98). The materials have been thoroughly characterized with respect to their structural and

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Fig. 1 Scheme showing nitroxide radicals intercalated into the layered Somasif host matrix. Depending on the orientation of the radical cations relative to the host layer, the layer-to-layer distance is subject to significant variations. Parts a to c show three possible scenarios, corresponding to parallel, transversal, and longitudinal orientations, respectively.

magnetic properties, using X-ray powder diffraction, magnetic susceptibility measurements, multinuclear solid state NMR and EPR spectroscopic techniques. In addition, the catalytic performance of these materials with respect to the oxidation of benzyl alcohol has been tested.

Experimental

Materials and synthesis

The host matrix clay used in this study is Somasif® ME100, a synthetic fluorohectorite clay produced by the CO-OP Chemical Co., Japan. This material belongs to the 2:1 type layered silicates (Fig. 2) and possesses a layer distance of 9.5 Å.⁸ The chemical formula can be expressed as $Na_{2x}Mg_{3.0-x}Si_4O_{10}$ -($F_{y}OH_{1-y}$)₂ (x = 0.15-0.5, y = 0.8-1.0),⁹ which corresponds to a



Fig. 2 Structure of the synthetic clay Somasif. Reprinted with permission from ref. 8.

cation exchange capacity (CEC) of 70 meq/100 g. The material used in the present study has x = 0.33 and y = 0.98 according to chemical analysis.⁸ The three radical species used are 4-(diethylmethylammonium)-2,2,6,6-tetramethylpiperidin-1-oxyl (abbreviated as DEMTEP, Fig. 3a) iodide and 1-[2-(4-amino-2,2,6,6-tetramethyl-1-piperidinyloxyl)-2-oxoethyl]-1'-methyl-4,4'-bipyridinium, chloride, iodide (1:1:1) (abbreviated as VIOTEP, Fig. 3b), as well as 2-(3-*N*-methylpyridinium)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl-3-*N*-oxide (*m*-MPYNN) iodide, (Fig. 3c, abbreviated as *m*-MPYNN).

DEMTEP and *m*-MPYNN were prepared following the reported methods.^{10–12} VIOTEP was readily prepared as described in Scheme 1. The educt 4-amino-2,2,6,6-tetramethyl-1-piperidinyloxyl and the precursor 4-[(2-chloroacetyl)amino]-2,2,6,6-tetramethyl-1-piperidinyloxyl were synthesized using standard literature procedures.^{13–15} The second and third steps of the reaction were prepared as follows.



Fig. 3 Lewis formulae of the radical species used in the present study: (a) 4-(diethylmethylammonium)-2,2,6,6-tetramethylpiperidin-1-oxyl (DEMTEP) iodide, (b) *m*-MPYNN cation, 2-(3-*N*-methylpyridinium)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl-3-*N*-oxide (*m*-MPYNN) iodide, (c) viologen tempo radical, 1-[2-(4-amino-2,2,6,6-tetramethyl-1-piperidinyloxyl)-2-oxoethyl]-1'-methyl-4,4'- bipyridinium, chloride, iodide (1 : 1 : 1) (VIOTEP).



1-[2-(4-Amino-2,2,6,6-tetramethyl-1-piperidinyloxyl)-2-oxoethyl]-4,4'-bipyridinium, chloride (1 : 1). In a sealed tube 4-[(2-chloroacetyl)amino]-2,2,6,6-tetramethyl-1-piperidinyloxyl (4.04 g, 16.35 mmol, 1.0 eq.) was dissolved in ACN and 4,4-bipyridine (2.80 g, 17.95 mmol, 1.1 eq.) was added. The reaction mixture was stirred overnight at 60 °C and afterwards poured in Et₂O (50 mL). The precipitate was filtered off and washed with EtOAc (3 × 5 mL). The product was obtained as a brown solid (4.07 g, 10.09 mmol, 62%). IR (film): 3376w, 3337w, 3198w, 3037m, 2932m, 1648s, 1639s, 1552s, 1461m, 1361m, 1303m, 1242m, 1087m, 976m, 816s, 609m cm⁻¹. HRMS (ESI) (*m/z*) calculated for [M]⁺: 368.2212, found: 368.2202.

1-[2-(4-Amino-2,2,6,6-tetramethyl-1-piperidinyloxyl)-2-oxoethyl]-1'-methyl-4,4'-bipyridinium, chloride, iodide (1:1:1). In a sealed tube 1-[2-(4-amino-2,2,6,6-tetramethyl-1-piperidinyloxyl)-2-oxoethyl]-4,4'-bipyridinium, chloride (1:1) (2.10 g, 5.22 mmol, 1.0 eq.) was dissolved in MeOH (5 mL) and methyliodide (1.6 mL, 25.69 mmol, 4.9 eq.) was added. The reaction mixture was stirred overnight at 60 °C and afterwards directly crystallized at -20 °C. The precipitate was filtered off and washed with Et₂O (3 × 10 mL). The product was obtained as a brown solid (2.85 g, 5.22 mmol, 99%). IR (film): 3436br, 3222w, 3039m, 2975m, 2931m, 1679s, 1638s, 1553m, 1504w, 1449m, 1346m, 1240m, 1102w, 974w, 828m, 548m cm⁻¹. HRMS (ESI) (*m*/*z*) calculated for [M]²⁺: 191.62180, found: 191.62185. Calculated for [M]⁺: 383.23968, found: 383.24420.

ESI-MS (m/z) and HRMS (m/z) were performed on a Bruker MicroTof or a Thermo Scientific Orbitrap LTQ XL. Infrared spectra were recorded on a Digilab Varian 3100 FT-IR Excalibur Series.

The ion exchange intercalation was carried out by stirring the clay in an aqueous solution of the radical salts for 4 hours at room temperature. Typically for one synthesis 200 mg clay was stirred in 20 mL of a 24 mM radical solution, which means 0.48 mmol of the radical, corresponding to 300% CEC. The product was filtered, washed until a colorless filtrate was obtained, and subsequently dried under vacuum (0.02 mbar) for 1–2 days. All the intercalation compounds are denoted as "Som(Radical), *x*% CEC", where *x* is the loading level.

Characterization

X-ray powder diffraction (XRD) was done on a Bruker D8 Advance diffractometer equipped with CuK_{α} radiation (λ = 0.154 nm). ¹H, ¹⁹F, ²³Na and ²⁷Al solid state NMR spectroscopic measurements were carried out on a Bruker DSX 500 spectrometer equipped with a 2.5 mm MAS NMR probe operating at a spinning speed of 30.0 kHz. ¹H, ¹⁹F and ²⁷Al MAS-NMR spectra were recorded at 500.13 MHz, 470.56 MHz and 130.33 MHz respectively, using 90° pulses of 1.6 to 4 µs length and a recycle delay of 1 s. ²³Na MAS-NMR spectra were measured at 132.2 MHz, using a 30° pulse of 0.9 µs length and a recycle delay of 2 s. ²⁹Si MAS-NMR spectroscopic measurements were carried out on an Apollo 300 spectrometer (resonance frequency 59.7 MHz) equipped with a 4 mm MAS NMR probe (MAS spinning frequency 10.0 kHz), using 90° pulses of 5 µs length and relaxation delays between 1 and 80 s. ²⁹Si and ¹⁹F spin lattice relaxation times were measured by the saturation recovery method. All the MAS-NMR lineshape deconvolutions were carried out using the DMFIT programme.¹⁶ Chemical shifts are reported relative to CFCl₃ (¹⁹F, using AlF₃ as a secondary standard), 1 M NaCl solution (²³Na), and tetramethylsilane (¹H, ²⁹Si), respectively. EPR measurements were conducted at room temperature on an EMS 104 EPR Analyzer from Bruker with an X-band (9.7 GHz) spectrometer (magnetic field strength 0.34 T) using the following conditions: microwave power between 10 and 25 mW, field sweep rate between 0.9 and 1.9 mT s^{-1} , field sweep range between 10 and 20 mT, modulation amplitude between 0.1 and 0.8 mT, modulation frequency 50 kHz. Magnetic susceptibility measurements were carried out at a magnetic field strength of 1 T, in the temperature range of 3-305 K using a Quantum Design Physical Property Measurement System (PPMS). All measurements were carried out using the VSM option by packing the powdered samples (9.437 mg Som(DEMTEP) 46% CEC, 6.761 mg Som(m-MPYNN) 71% CEC, 7.019 mg Som(m-MPYNN) 20% CEC and 6.918 mg Som(VIOTEP) 62% CEC) in polypropylene capsules and attaching them to a sample holder.

Catalytic studies

The immobilized TEMPO ammonium salt (1.5–20 mol% with respect to the amount of substrate) was added to a reaction

vessel which was equipped with a frit to filter off the reaction mixture directly. A solution of the alcohol (0.50 M, 1.0 equiv.) in CH₂Cl₂, a solution of KBr (aq., 0.50 M, 10 mol%) and a solution of NaOCl (1.25 eq.) and NaHCO₃ (approx. 10 mg, pH = 9.0) were added at 0 °C. The reaction mixture was shaken for 3 h at 0 °C. The catalyst was filtered off from the reaction mixture, washed with CH₂Cl₂ (2 × 2 mL) and the conversion was determined by means of gas chromatography using a Hewlett-Packard GC HP6890-1 (30 m × 0.25 µm) column and a GC Agilent Technologies 7890A (30 m × 0.25 µm) column with hydrogen at about 1 bar. Subsequently the procedure was repeated up to 40 times, every time by re-exposing the catalyst material to a fresh reaction mixture.

Results and discussion

Guest-host interactions

Guest species uptake. The amount of the intercalated radical (reported in units of % CEC) was quantified *via* CHN elemental analysis. The level of intercalation *x* can be calculated from the measured radical content (in wt%) using the following formula:⁵

$$x = \frac{\text{wt}\%_{\text{radical}} M_{\text{somasif}}}{M_{\text{radical}} - \text{wt}\%_{\text{radical}} (M_{\text{radical}} - M_{\text{NA}})}$$

Fig. 4 shows the uptake curve as a function of the amount of the radical offered in the solution. The horizontal axis is defined as the molar ratio of the offered radical cation in the original solution to the total sodium content in the host matrix ($n_{\text{radical}}/n_{\text{Na}+}$). The ordinate shows the amount *x* of the intercalated radical in the host structure. Both curves in Fig. 4 demonstrate that by increasing the amount of the radical offered, the amount of intercalated material can be increased until a saturation value around 30% CEC for Som(DEMTEP) and 70% CEC for Som(*m*-MPYNN) is reached, even with high



Fig. 4 Uptake curves of the radicals *m*-MPYNN and DEMTEP, determined by CHN elemental analysis, intercalated into Somasif under the conditions described in the text.

excess of the radical offered. Higher loadings (46% CEC) of DEMTEP could be realized by using a 40 mM radical solution with doubly-distilled water as a solvent and stirring for 5 hours.

Guest species orientation inferred from X-ray powder diffraction. Fig. 5a-c summarize the X-ray powder diffraction



Fig. 5 X-ray powder diffraction pattern of (a) Som(*m*-MPYNN), (b) Som-(DEMTEP) (bottom) at different levels of intercalation, and (c) of Som(VIOTEP) before and after 20 subsequent catalytic conversions.

Table 1Intercalation degree [$\pm 2\%$ CEC], layer-to-layer distance d(001) andinterlayer spacing (± 0.2 Å) of the intercalation compounds investigated

	Intercalation degree [% CEC]	<i>d</i> (001) [Å]	Interlayer spacing [Å]	Corresponding arrangement
Som(<i>m</i> -MPYNN)	series			
1	8	9.6	2.6	(Na^+)
		12.2	5.2	Parallel
2	20	14.8	7.8	Transversal
3	42	15.0	8.0	Transversal
4	51	15.2	8.2	Transversal
		18.9	11.9	Longitudinal
5	61	17.2	10.2	Disordered
				(transversal/
				longitudinal)
6	71	18.9	11.9	Longitudinal
Som(DEMTEP) se	eries			0
1	7	12.1	5.1	Parallel
2	21	14.6	7.6	Transversal
3	30	14.6	7.6	Transversal
4	32	14.7	7.7	Transversal
5	33	14.6	7.6	Transversal
6	35	14.6	7.6	Transversal
7	46	14.7	7.7	Transversal
		17.5	10.5	Longitudinal
Som(VIOTEP)	56	15.9	8.9	U
After 20 catalytic cycles	~10	12.6	5.6	

data obtained on all intercalated compounds. For the pure host compound, the (001) reflection appears at d = 9.5 Å, which corresponds to the layer-to-layer distance. From this value, the size of the interlayer gap can be deduced to be 2.5 Å. As illustrated in Fig. 5 and Table 1, the (001) reflection is significantly shifted in the intercalated materials, revealing substantial expansions of the layer-to-layer distance for the materials studied. In the case of the *m*-MPYNN intercalation compounds, Fig. 5a shows that with increasing intercalated radical contents the layer-to-layer distance changes continuously from 12.2 Å to 18.9 Å, corresponding to a continuous increase of the size of the interlayer gap from 5.2 Å to 11.9 Å, at the lowest and the highest radical contents, respectively. By comparing the extent of the interlayer expansion with the guest species's molecular dimensions, information about the guest species orientation relative to the layers can be deduced. To this end, the molecular dimensions were estimated from furthest interatomic distances in each dimension, as measured from the crystal structure, using the program DIAMOND. In doing so, the molecules were approximated as rigid species without internal mobility. For the *m*-MPYNN radical, with estimated molecular dimensions of $9.8 \times 5.8 \times 4.6$ Å, the orientation of the radicals within the layers can be considered as almost longitudinal, i.e. with the long axis of the molecule perpendicular to the layer (Fig. 1c) for the samples with 71% CEC while for the samples with lower degrees of intercalation, the parallel and transversal orientations appear to be preferred. The 51% CEC sample shows almost equal contents of domains with longitudinal and transversal orientations. The d spacing of the 61% CEC sample is in between both orientations. In view of the enhanced half width, one can

assume a considerable extent of disorder. The broad reflection (tailing) of the 20% CEC sample indicates a distribution of domains with parallel and transversal orientations in the manner as shown in Fig. 1a and b as well as domains with incomplete loading.

Fig. 5b shows the results for the DEMTEP intercalation compounds. Again, the layer-to-layer distance tends to increase with increasing radical loading level, even though the changes appear less gradual. At the lowest loading (7% CEC) the layerto-layer distance is 12.1 Å, corresponding to an interlayer gap size of 5.1 Å. Within the concentration range 21-33% CEC, a constant laver-to-laver distance of 14.6 Å is observed, corresponding to an interlayer gap of 7.6 Å. As the DEMTEP radical ion has the estimated molecular dimensions of 8.7 \times 6.3 \times 4.6 Å, these two interlayer gap sizes are most consistent with a parallel arrangement at the lowest concentration and a transversal orientation in the intermediate concentration range. The Som(DEMTEP) sample with the highest degree of intercalation (46% CEC) shows in addition to the 14.6 Å distance also larger distances up to 17.5 Å, which suggests certain layers with transversal and other layers with longitudinal intercalation, similar to the 51% CEC m-MPYNN sample.

Fig. 5c shows the XRD data of the VIOTEP radical intercalate. Here the expansion of the layer-to-layer distance of 15.9 Å (interlayer gap 8.9 Å) allows no straightforward conclusion about the orientation, as the molecular dimensions are not known owing to the absence of a crystal structure. The diffraction pattern observed for the material following 20 successive runs is also shown. For this material, the expansion is seen to be considerably diminished (12.6 Å), consistent with a significantly altered orientation distribution of those VIOTEP molecules still retained within the host structure at this stage. The very broad diffraction peaks indicate a distribution of domains with different degrees of intercalation, a consequence of the leaching (*vide infra*).

²³Na, ¹⁹F, and ²⁹Si solid state NMR spectroscopy. Solid state NMR spectroscopic studies of the constituent nuclei in the host structure were conducted to probe the interactions between the paramagnetic guest species and the Somasif slabs. Fig. 6a shows the ²³Na MAS-NMR signals of the pure host material and the three hybrid materials Som(DEMTEP), Som(m-MPYNN) and Som(VIOTEP), all of which have the highest degree of intercalation realized. Somasif samples have been shown previously to yield three spectroscopically distinct ²³Na resonances:⁸ the signal near 38 ppm (isotropic chemical shift δ_{CS}^{iso} = 41.7 ppm, SOQE = 1.6 MHz) is assigned to nonexchangeable sodium ions on the Mg positions within the aluminosilicate slabs. The resonance near -22.0 ppm (δ_{CS}^{iso} = -19.8 ppm, SOQE = 1.5 MHz) arises from exchangeable nonhydrated Na⁺ ions found in the interlayer space. Furthermore, a weaker signal characterized by $\delta_{CS}^{iso} = -2.3$ ppm, SOQE = 2.9 MHz can be assigned to (at least partially) hydrated exchangeable Na⁺ ions in the interlayer space. Fig. 6a shows that in the intercalation compounds having the maximum degree of intercalation, only the non-exchangeable Na⁺ ions remain. Fig. 6a also includes a spectrum of a Som(VIOTEP)



Fig. 6 ²³Na MAS-NMR spectra of the intercalation compounds: (a) comparison between the different systems at their maximum respective intercalation levels, (b) comparison between different intercalation levels for the Som(*m*-MPYNN) series, (c) comparison between different intercalation levels for the Som-(DEMTEP) series.

sample exposed to 20 catalytic cycles. From chemical analysis it is known that this sample has been partially leached and thus contains significantly lower concentrations of radical ions. Indeed, the ²³Na NMR spectrum indicates that this leaching effect has restored part of the sodium occupancies in the exchangeable interlayer sites. The spectroscopic parameters indicate that this sodium is mostly of the hydrated type. In addition, a strong signal near 7.0 ppm can be attributed to

surface adsorbed sodium ions species from the NaOCl electrolyte solution used in the catalytic reaction. Fig. 6b and c show the ²³Na MAS-NMR spectra of the Som(m-MPYNN)- and Som(DEMTEP)-series as a function of the amount of the intercalated radical. As expected the resonance line near -22.0 ppm decreases monotonically as the degree of intercalation is increased. The data illustrate that ²³Na MAS-NMR spectroscopy could be a convenient tool for monitoring the progress of the ion exchange reaction. In the case of the DEMTEP and *m*-MPYNN intercalates the near-disappearance of the low-frequency signal at the highest intercalation levels suggests that virtually no exchangeable sodium ions remain in the interlayer space. This is not, however, what is expected based on the CEC values. Indeed, closer inspection of the signals reveals a broad signal component due to hydrated Na⁺ ions, which is difficult to quantify. It is also possible that part of the residual Na⁺ ions in the interlayer space do not contribute to the spectrum, as their line shapes may be broadened beyond detectability by paramagnetic interactions with nitroxide radical ions in their vicinity. In contrast, the line shapes of the non-exchangeable Na⁺ ions appear completely unaffected by paramagnetic broadening, suggesting that these ions are indeed spatially remote from the interlayer space. These uncertainties make it difficult to quantify the degree of intercalation on the basis of the integrated ²³Na NMR peak area ratio of the non-exchangeable and the exchangeable Na⁺ ions. While the corresponding analysis was attempted and indeed reveals the expected general trend, the scatter observed by this analysis is significantly stronger than that obtained from the chemical analysis data. Hence the latter method must be considered superior to the ²³Na NMR MAS peak integration in determining the extent of ion exchange achieved.

Fig. 7 presents the ¹⁹F MAS-NMR spectra of the intercalation compounds with *m*-MPYNN and DEMTEP. As previously discussed, the complex spectrum that is observed in the pure host material reflects the presence of multiple F environments with different numbers of Mg²⁺ ions, Na⁺ ions and vacancies within their first coordination spheres.8 For the *m*-MPYNN-series (Fig. 7a) the presence of the radical species in these samples has no strong spectroscopic consequences aside from a significant shortening of the spin-lattice relaxation times T_1 (Table 2). In contrast, Fig. 7b shows that in the case of the DEMTEP-intercalates the ¹⁹F MAS NMR line shapes are significantly broadened and a drastic shortening of the T_1 values is also observed. Thus, these results suggest that electron spin-host structure interactions in the DEMTEP intercalation compound are significantly stronger than in the *m*-MPYNN intercalate, despite the fact that the DEMTEP species are present at considerably lower concentrations.

The ²⁷Al MAS-NMR spectra (data not shown) reveal single peaks, with isotropic chemical shifts (67 ppm vs. 1 M aqueous Al(NO₃)₃ solution) typical of four-coordinate Al species. No changes are detectable upon nitroxide intercalation. Finally, the principal ²⁹Si MAS-NMR signals (Fig. 8) of the hybrid materials also show no noticeable changes in the position of the dominant line (-95 ppm), whereas the minority line

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Fig. 7 19 F MAS-NMR spectra and spin-lattice relaxation times of (a) the Som-(*m*-MPYNN) and (b) the Som(DEMTEP) series with different compositions.

Table 2 ²⁹Si and ¹⁹F spin-lattice relaxation times T_1 of the pure host material Somaif and the hybrid materials Som(*m*-MPYNN), Som(DEMTEP) and Som-(VIOTEP)

Sample	¹⁹ F <i>T</i> ₁ [ms]	²⁹ Si <i>T</i> ₁ [ms]	
Somasif	8635s (±226)	29 679 (±2506)	
Som(m-MPYNN)		()	
8% CEC	472 (±77)		
20% CEC	$60(\pm 11)$	355 (±35)	
42% CEC	22 (±4)	116 (±9)	
51% CEC	25 (±5)	$119(\pm 23)$	
61% CEC	22 (±5)	216 (±18)	
71% CEC	45 (±8)	575 (±60)	
Som(DEMTEP)		()	
7% CEC	285 (±77)		
21% CEC	31 (±7)	$40(\pm 3)$	
30% CEC	$15(\pm 4)$	23 (±3)	
32% CEC	$15(\pm 4)$	24 (±4)	
33% CEC	12 (±3)	75 (±21)	
46% CEC	8 (±2)	16 (±2)	
SOM(VIOTEP)			
56% CEC	$109(\pm 16)$	89 (±7)	
~10% CEC	872 (±48)	7075 (±1150)	

(-98 ppm) is not visible in the intercalates. There are no systematic trends in the ²⁹Si NMR line widths (about 5 ppm) upon intercalation, but there is a significant shortening of the



Fig. 8 $^{29}{\rm Si}$ MAS-NMR spectra of pure Somasif and the intercalation compounds with different systems.

spin lattice relaxation times T_1 (Table 2). Again these effects are more pronounced for the DEMTEP than for the *m*-MPYNN intercalates. However, in the case of the *m*-MPYNN intercalates, Table 2 reveals a remarkable anomaly: with increasing radical ion content the value of T_1 initially shows the expected decrease, passes through a minimum near 42-51% CEC and increases again towards higher loading levels, despite the increased spin concentration. A plausible explanation for this anomaly is based on Fig. 9, which illustrates that the three distinct intercalation scenarios present different distances between the spin-carrying nitroxide groups of the *m*-MPYNN radical cations and the silicon layers in the host matrix. Specifically, the N-O groups are most closely situated towards the layers in the transversal intercalates, while in the parallel and longitudinal orientation they are much more remote. Thus, the influence of the electron spin centre on the ²⁹Si layers is expected to depend on the arrangement of the radical cations. Indeed, Table 2 reveals that the spin-lattice relaxation times go through a minimum at those compositions at which the fraction of molecules with transversal orientation reaches a maximum. In contrast, in the DEMTEP intercalation compounds, where no close approach of the nitroxide group to the silicate slabs is expected for the transversal intercalation, the experimental trend in the ²⁹Si spin lattice relaxation times just reflects (roughly) the expected dependence on overall spin concentration.

Guest-guest interactions

Magnetic susceptibility and EPR measurements. To test for cooperative magnetic ordering effects the bulk magnetic properties have been measured for four representative intercalation compounds. To eliminate the contribution from the Somasif host, the experimental χT versus T curve for the latter has been subtracted from the data obtained on the intercalation compounds. The resulting curves are shown in Fig. 10 and fitted to the expression $\chi T = \chi_0 T + CT/(T - \Theta)$. In this expression χ_0 comprises the effect of the temperature independent diamagnetic and van-Vleck paramagnetic contributions, C is the Curie



Fig. 9 A schematic description showing the different distances between the nitroxide groups on the *m*-MPYNN radical molecules and the silicon layer in the host matrix depending on the orientation of the radical cations relative to the host layer: (a) parallel, (b) transversal, (c) longitudinal.



Fig. 10 Plot of the product of molar magnetic susceptibility and temperature, χT , versus temperature for representative Somasif intercalation compounds subject to the present study.

constant, and Θ is the Weiss constant characterizing cooperative ordering effects. Table 3 summarizes the parameters obtained. All the data are consistent with dominant Curie-Weiss behavior. Based on the known radical ion concentrations the molecular magnetic moments of the radical species can be determined from the C values obtained: they fall between $1.77\mu_{\rm B}$ and $1.66\mu_{\rm B}$, for the DEMTEP and the m-MPYNN intercalates, respectively, corresponding closely to the theoretically expected value of $1.68\mu_{\rm B}$.¹⁷ A substantially lower value of $1.11\mu_{\rm B}$ is measured for the VIOTEP intercalate. This result could arise from diamagnetic impurities or from some clustering of the intercalated VIOTEP radical species. For all the intercalated systems studied, the dominant Curie-Weiss behavior observed indicates the absence of cooperative magnetic interactions. We thus conclude that the strategy of confining these radical cations into the interlayer space of clay materials does not lead to cooperative magnetic phenomena in the bulk, consistent with earlier results from our laboratory.4,5

Compound	$\mu_{\rm eff}$ ($\mu_{\rm B}$ /f.u.)	$\theta_{\mathrm{P}}\left(\mathrm{K}\right)$	$\chi_0 (\mathrm{emu} \mathrm{mol}^{-1})$
Som(DEMTEP) 46% CEC Som(<i>m</i> -MPYNN) 71% CEC Som(<i>m</i> -MPYNN) 20% CEC Som(VIOTEP) 62% CEC	$1.71(1) \\ 1.66(1) \\ 1.77(1) \\ 1.10(1)$	$\begin{array}{c} -0.4(5) \\ -1.9(5) \\ 0.6(5) \\ 2.0(5) \end{array}$	$\begin{array}{c} 9.32(1)\times 10^{-6} \\ 6.63(1)\times 10^{-5} \\ -1.48(1)\times 10^{-4} \\ 1.21(1)\times 10^{-4} \end{array}$

Representative intercalation compounds were also studied by EPR spectroscopy. The spectra measured on the *m*-MPYNN intercalation compounds show a symmetric signal at g = 2.007(see Fig. 11). In all of the materials studied, the peak structure expected from the anisotropic magnetic hyperfine coupling with the ¹⁴N nuclei is averaged out owing to rapid spin-state fluctuations caused by strong intermolecular electron-electron interactions. The line width of this resonance shows a systematic dependence on radical content, suggesting that the rate of these spin state fluctuations increases with increasing levels of intercalation (motional narrowing effect). Such behaviour would be expected for the case of a random distribution (absence of clustering) of the radical species. An interesting deviation from this monotonic behaviour is observed in the DEMTEP series at the lowest intercalation level studied. Here the line width appears narrower than expected on the basis of a random spin distribution, suggesting some extent of clustering. This observation may be related to the parallel orientation of the radical ion relative to the Somasif layers seen at this low ion concentration, which is distinctly different from the orientation at higher loadings. Finally, the spin state fluctuations among neighboring electron spins are the fastest in the pure radical ion salts, producing the narrowest lines within each of the compositional series investigated.

¹H MAS-NMR spectroscopy. Fig. 12a and b show high speed ¹H MAS-NMR spectra of the pure host material, the pure radical ion salts, as well as of their intercalation compounds as a function of composition, for both the *m*-MPYNN and the DEMTEP series. For the pure host material, one sharp signal

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Fig. 11 X-Band EPR spectra of (a) Som(*m*-MPYNN) and (b) Som(DEMTEP) intercalation compounds depending on the degree of intercalation, (c) and (d) EPR line widths as a function of the degree of intercalation for both systems.

at 4.0 ppm is observed, which arises from H₂O molecules present in the interlayer space. The spectra of the intercalation compounds (and of the pure radical molecular ions) are significantly affected by paramagnetic shift and broadening effects, reflecting the spin density distributions in the molecule as well as intermolecular interaction effects. Large paramagnetic shifts have been observed for paramagnetic materials of great chemical diversity including organic radicals,^{19,20} biological solids²¹ and doped inorganic materials.^{22,23} Deconvolution results, including the corresponding peak assignments, are summarized in Table 4. Note that the spectra of the pure radical ion salts appear to be substantially better resolved than those of the intercalation compounds. This effect can be explained on the basis of the motional narrowing effects evident in the EPR spectra. Very fast spin state fluctuations such as those present in the pure radical ion salts produce an average electronic environment for the proton nuclei, reflecting the local spin density distribution in the molecule, averaged according to the electron spin state populations governed by the Boltzmann distribution. The spectra of the intercalation compounds are significantly less-well resolved and reveal substantial line broadening effects, particularly in the *m*-MPYNN intercalate at low loadings. For this series of intercalation compounds, there appears to be a clear correlation between line broadening effects and guest species orientation, suggesting that intermolecular radical-radical interactions are weaker in the transversal intercalates. The peak positions (Fig. 12a and Table 4) reflect the spin density distributions within the radical cation

molecule.^{19,20} Only minor variations in resonance shifts are observed for a given guest species moiety. This indicates that the molecular spin distribution is not much different from that observed in the pure radical cation salt, and is also not much influenced by the guest species orientation. The biggest chemical shift discrepancy is observed for the N-methyl group (13.2 ppm in the intercalate vs. 15.3 ppm in the pure radical cation iodide), but this effect could also be attributed to a chemical shift contribution arising from the interaction of the positively charged nitrogen atom with the anionic Somasif slabs. While paramagnetic and chemical shift contributions can be separated in principle by variable temperature measurements,¹⁹⁻²¹ the spectroscopic resolution observed in the present intercalation compounds is not sufficient to provide the necessary measurement precision. Similar conclusions were previously reached for a number of radical intercalation compounds in saponites.⁴ For the DEMTEP intercalate (Fig. 12b), the biggest difference with respect to the DEMTEP iodide salt is the absence of the low-frequency shifted signals attributed to the β -methyl groups, except at the highest intercalation level (46% CEC) where an extremely broad component may be perceived. Again, we attribute the disappearance of these signals to a slowing down of the electronic spin state fluctuations evidenced from the EPR spectra, because the intermolecular electron-electron interactions are weakening as the loading level is decreased. Unfortunately a detailed analysis of the peak positions is not possible in this case, because of strong overlap with the background signal from the host structure.



Fig. 12 ¹H MAS-NMR spectra of (a) the Som(*m*-MPYNN) series, (b) the Som-(DEMTEP) series. Each plot includes reference spectra of the pure host and the pure radical cation salts. Spinning sidebands are marked with asterisks.

Catalytic activity

The hybrid materials Som(DEMTEP) and Som(VIOTEP) can be used as recyclable catalysts for the oxidation reaction of benzyl alcohol to benzaldehyde (Scheme 2). In contrast, the empty



Scheme 2 Catalyzed oxidation of benzyl alcohol studied in the present manuscript.

host material is unreactive under comparable experimental conditions (<26% conversion), and Som(m-MPYNN) intercalates were found to be unsuitable as they resulted in decomposition reactions.

Fig. 13 shows the conversion during the first 20 subsequent catalytic reactions using both hybrid materials at a catalyst concentration of 4 mol% with respect to the substrate. Within experimental error, the performances of both catalysts are comparable up to 20 cycles. Experiments with lower catalyst-tosubstrate ratios gave similar results; however, catalytic activity tends to cease more quickly (data not shown). With higher ratios, up to 40 cycles could be reached with the VIOTEP system (data not shown). The catalytic activity of spent catalytic materials after 20-40 reaction cycles can be restored by reexposing them to a fresh aqueous solution of the radical cation salt. As shown in Fig. 14, this process can be monitored by EPR spectroscopy. While the spectra of the original and reloaded catalysts are broadened by strong dipolar and exchange interactions, reflecting the considerably enhanced magnetic dipole-dipole interactions in these higher-concentrated materials, the spectra observed in the spent catalysts, where the radical species are rather dilute, are typical of isolated nitroxide radicals, allowing the resolution of anisotropic g-values and hyperfine coupling constants.²⁴ From the spectrum shown in Fig. 14b for Som(VIOTEP), the following parameters can be determined using Matlab Easy Spin library:¹⁸ g_{xx} = 2.006681, g_{yy} = 2.005302, g_{zz} = 2.001715 and for the A-tensor: A_{xx} = 12.65204 mT, A_{yy} = 26.1093 mT, A_{zz} = 96.63939 mT. Clear differences between leached and re-loaded catalysts are also seen in the ²³Na NMR spectra (see Fig. 9) and the ¹H MAS-NMR spectra (data not shown) in agreement with previous studies of TEMPO-loaded saponites.6

 Table 4
 ¹H MAS-NMR fits and peak assignments (in ppm ± 0.5 ppm unless specified otherwise) obtained for the spectra of the pure radical ion salt and representative intercalation compounds

Sample	Aromatic		<i>N</i> -Methyl	β -Methyl
<i>m</i> -MPYNN Som(<i>m</i> -MPYNN) 71% CEC	50.5; 44.9 (2); -4.5 47.1 (2); 38.8; -2.5		15.3 13.2	-8.1; -12.8 (2); -14.2 -11.1; -12.7
	N–R-group		Ring-CH ₂	β -Methyl
DEMTEP Som(DEMTEP) 46% CEC	3.6; 2.9; 2.0; 1.4 5.0; 2.1		-8.9; -15.2 	-25.2; -27.5 -27 ± 2
	Viologen-group	N-R-group	Ring-CH ₂	β -Methyl
VIOTEP Som(VIOTEP) 56% CEC Som(VIOTEP) after 20 cycles ~10% CEC	10.2; 9.2 9.1; 8.6 9.1; 7.9	4.5; 3.5; 2.0; 0.8 4.8; 3.1; 1.7; 0.9 4.5; 3.6; 1.1	-16.3 	-27.5



Fig. 13 Catalysis conversion degree against the cycle number for the two hybrid samples (a) Som(DEMTEP) 46% CEC and (b) Som(VIOTEP) 56% CEC.



Fig. 14 (a) EPR spectra of (from top to bottom, a1 to a5): (a1) DEMTEP iodide, (a2) Som(DEMTEP) 33% CEC, before catalytic use, (a3) sample (a2) following 20 catalytic runs (catalyst level 4 mol% of the amount of substrate samples), (a4) sample (a2) following 40 catalytic runs (catalyst level 20 mol% of the amount of substrate samples) and (a5) sample (a4) following re-loading by exposure to 10 mL of a 16 mM solution of DEMTEP iodide for 4 h. (b) EPR spectra of (from top to bottom b1 to b4): VIOTEP iodide chloride, (b2) Som(VIOTEP), 56% CEC, before catalytic use, (b3) sample (b2) following 20 catalytic runs (catalyst level 20 mol% of the amount of substrate samples) and (b4) sample (b3) following re-loading by exposure to 15 mL of a 16 mM solution of DEMTEP iodide for 4 h.

Conclusions

In summary, a series of new inorganic-organic hybrid materials based on a layered synthetic fluoromica host material with three different stable radicals has been prepared via an ion exchange reaction and has subsequently been characterized. ²³Na MAS-NMR spectroscopy is well-suited to monitor the depletion of the Na⁺ ions in the interlayer space caused by the ion exchange process. The expansion of the host matrix layer distance can be correlated with the molecular dimensions of the radical cations, suggesting various different orientations of these species in the interlayer space. While solid state ²⁹Si and ¹⁹F MAS-NMR spectra indicate that radical intercalation does not affect the local environments of the atoms in the layered slabs of the host structure, their spin relaxation times probe the proximity of the spin carrying moieties and are therefore sensitive to molecular orientation effects. Systematic compositional trends in the line widths of the EPR spectra and the solid-state ¹H MAS-NMR spectra indicate that the intermolecular electron spin exchange rates are concentration dependent. In addition, trends in the resonance shifts suggest that the spin density distributions are modified by intermolecular electron-electron interactions among neighboring radical cation species. However, no bulk magnetic ordering is observed, consistent with only weak intermolecular interactions among the electron spins. For the oxidation of benzyl alcohol to benzaldehyde, a typical model reaction, the DEMTEP and VIOTEP intercalates reveal high reactivity during the first twenty cycles.

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