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Introduction

Since the early days of heterogeneous catalysis, scientists have tried to mimic nature in designing catalysts with ever higher conversion and selectivity. Hybrid materials, formed by the combination of inorganic and organic building units, are attractive for the purpose of creating high-performance or highly functionalized structures.^{1–3} Combining the advantages of inorganic solids (high mechanical, thermal, and structural stability) and organic molecules or macromolecules

Acid properties of organosiliceous hybrid materials based on pendant (fluoro)aryl-sulfonic groups through a spectroscopic study with probe molecules[†]

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Two different heterogeneous catalysts carrying aryl-sulfonic moieties, in which the aromatic ring was either fluorinated or not, were successfully synthesized. The multi-step synthetic approaches implemented involved the synthesis of the silyl-derivative, template-free one-pot co-condensation (at low temperature and neutral pH) and tethering reaction. A multi-technique approach was implemented to characterize the hybrid organic-inorganic catalysts involving TGA, N₂ physisorption analysis, FTIR spectroscopy, and ss MAS NMR (¹H, ¹³C, ²⁹Si) spectroscopy. Specifically, the acidity of the organosiliceous hybrid materials was studied through the adsorption of probe molecules (*i.e.* CO at 77 K and NH₃ and TMPO at room temperature) and a combination of FTIR and ss MAS NMR spectroscopy. The catalytic activity of the two hybrids was tested in the acetal formation reaction between benzaldehyde and ethylene glycol. Preliminary results indicated superior performances for the fluoro-aryl-sulfonic acid, compared to the non-fluorinated sample. The findings hereby reported open new avenues for the design of heterogeneous sulfonic acids with superior reactivity in acid-catalyzed reactions. Moreover, through the implementation of spectroscopic studies, using probe molecules, it was possible to investigate in detail the acidic properties of hybrid organosiliceous materials.

(flexibility and functionality), they are suitable for a wide range of applications, including catalysis,⁴ adsorption,⁵ separation,⁶ microelectronics,⁷ and photoluminescence.8 Organosilica-based materials are by far the most used supports to develop type II⁹ hybrid catalysts,² due to the simplicity of their synthesis, their tuneable textural properties and their highly reactive surface, which make them ideal platform supports for grafting or tethering additional active sites.¹⁰ Among the different approaches to incorporate organic moieties into inorganic frameworks,² sol-gel chemistry, in particular the co-condensation of a mixture of siloxanes together with organo-silanes, is one of the most commonly used.¹¹⁻¹³ Interestingly, one-pot synthesis methods of several hybrid organic-inorganic materials by fluoride-catalysed synthesis have been described in the literature.¹² This strategy offers numerous advantages such as low synthesis temperatures, nearly neutral pH and the absence of templating agents, at the same time providing final porous materials with a high surface area and tuneable porosity.¹⁴ The purely siliceous solids obtained present a high surface area (up to 1000 m² g⁻¹) and a nonordered system of mesopores (so-called NOS-type materials). These properties, together with a highly reactive surface,



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make them ideal platform systems for developing novel supported hybrid organic–inorganic catalysts. In order to covalently bond the organic molecule with the silica framework, the former needs to be functionalized with an alkoxy-silyl group that will eventually undergo hydrolysis/condensation, together with the silica precursors.^{15–17}

Sulfonic acids are one of the many functional groups that have been used to prepare silica-based heterogeneous organocatalysts bearing strong acid sites¹⁸ for carrying out esterification of fatty acids,¹⁹ acetalization reactions,²⁰ and acetal hydrolysis.²¹ The effect of nearby atoms on the catalytic activity of sulfonic acids has been studied and industrially exploited for several decades. For example, propyl- and arylsulfonic acids were supported on amorphous silica and their activity was compared in the reaction of anisol with acetic anhydride,²² showing a beneficial effect of having the sulfonic group bound to an aromatic ring. Fluorinated alkylsulfonic acids show an even more representative example of the effect of the chemical makeup of the sulfonic acid on the catalytic activity.²³⁻²⁶ The inductive effect provided by having fluorine as a substituent on the carbon in the α position greatly enhances the acidity of the proton. Nevertheless, the synergistic effect of having the sulfonic group bound to a fluorinated aromatic ring has not been deeply explored taking into account the interaction of acid active groups with the silica surface. In this work, we report the synthesis of supported arylsulfonic acid organocatalysts on NOS-type materials. To investigate the inductive effect of fluorine on the aryl-sulfonic groups and, ultimately, on acidity, two different catalysts were designed and compared. In one of them the aromatic ring was fluorinated, while in the other it was not. The two hybrid materials underwent in-depth physico-chemical characterization aimed to study their morphology, textural properties, thermal stability and spectroscopic properties. Specifically, a combination of FTIR and multinuclear solid state NMR methods was implemented. Additionally, probe molecules of different basic strengths were adsorbed/desorbed onto the hybrids. Gaseous or highly volatile bases such as carbon monoxide, ammonia, pyridine and pyridine derivatives have been widely used as probe molecules to study the acidic properties of purely inorganic catalysts.²⁷⁻²⁹ Nevertheless, within the field of organosiliceous hybrid catalysts, this insightful characterization approach remains unexplored. In this study, for the first time, carbon monoxide and ammonia were adsorbed on the surface of the hybrids and their interaction was followed both by FTIR and ss NMR spectroscopy in order to assess the acidity of the hybrid catalysts. The results obtained from this characterization study were decisive to better explain the catalytic activity in solid-acid-catalysed reactions.

Results and discussion

To modulate the acid strength in sulfonic hybrid catalysts, two different organic moieties containing protonated or fluorinated aryl-sulfonic acid groups were developed. The synthesis of the two hybrid catalysts containing aryl-sulfonic groups was carried out following two different approaches (Scheme 1). In the case of the hybrid with a protonated aromatic ring named HSO₃-NOS-H (A), sulfanilic acid was firstly reacted with NaOH to achieve its sodium form (1) and enhance its solubility in acetonitrile. The silvl derivative carrying the sodium sulfonate group (compound 2) was obtained through the reaction of the primary amine present on the phenyl ring of 1 with 3-(triethoxysilyl)propyl isocyanate (acetonitrile, 65 °C, N₂), which led to the formation of the urea group as indicated in the liquid (¹H and ¹³C) NMR spectra (Fig. S1 and S2[†]). The peaks observed were consistent with the desired product; specifically, the ¹³C signal centred at 160 ppm is typical of the carbonyl carbon in the urea group. The synthesis of the heterogeneous catalyst was achieved by cocondensation of 2 and tetramethyl orthosilicate (TMOS), carried out in methanol and water (1:1). Hydrolysis and condensation of the alkoxy groups were catalysed by F⁻ ions, which acted as mineralizing agents.¹²

As mentioned above, this approach presents several advantages, such as the synthesis was carried out at 36 °C, for 24 h, under mild pH conditions, using low amounts of solvent and catalyst. Moreover, the textural properties (specific surface area and mean pore size) could be tuned by varying the F⁻ concentration and the chain length of the alcohol used as a co-solvent.¹² The synthesis of the hybrid with a fluorinated aromatic ring named HSO3-NOS-F (B) was carried out using a slightly different approach (Scheme 1). Substrate 5 was found insoluble in any solvent besides H₂O and DMSO. Implementing the former would have been detrimental to the alkoxy groups of the silyl-derivative. Using the latter would have required a very high temperature for its distillation. Such a high temperature might promote the spontaneous condensation of the alkoxy groups of the organosilane compounds and their partial polymerization. To avoid this problem, a Br-propyl functionalized NOS was first synthesized. Afterwards, the solid was reacted with 5, previously with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) to mixed



Scheme 1 Representation of the synthesis of the supported sulfonic acids: (A) HSO₃-NOS-H and (B) HSO₃-NOS-F.

promote the deprotonation of the hydroxyl group, leading to a non-porous hybrid material with pendant (fluoro)aryl-sulfonic groups (6).

In both synthetic pathways, the exchange of sodium with a proton was achieved by suspending 3 and 6 in an HCl solution in EtOH. The total exchange of Na was checked by ICP analysis. HSO₃-NOS-H and HSO₃-NOS-F underwent in-depth physico-chemical characterization. Firstly, thermogravimetric analysis was conducted on both samples to measure the organic content and to probe the thermal stability of the materials. The weight losses (TGA) and the respective DTA curves of the materials are reported in Fig. 1. The first weight loss experienced by both materials occurs between 70 and 150 °C and it's associated with the removal of physisorbed water (I). Focusing on HSO₃-NOS-H (curves a and a'), a second weight loss is observed between 250 and 380 °C (II). This is probably due to the breakage of the urea bond and consequent desorption of the phenyl-sulfonic moieties.²¹ Finally, the loss between 500 and 600 °C is due to the decomposition of the propyl chain anchored to the surface (III). Considering this as the limit temperature for the total decomposition of the organic moieties supported on silica, the loss was found to be about 15% of the overall weight (temperature range between 200 and 600 °C). Shifting to HSO3-NOS-F (curves b and b'), after the initial loss due to the desorption of physisorbed water, a main weight loss due to the organic moieties is observed at about 300-450 °C and it is related to the breakage of the ether bond linking the fluorinated phenyl ring to the propyl chain (IV). Lastly, the weight loss between 500 and 600 °C was attributed to the thermal decomposition of the alkyl chains, still anchored to the silica surface (V). The total weight loss due to the organic moieties was about 8.4% of the total weight. In both hybrid solids, a progressive weight loss at temperatures above 600 °C was detected due to dehydroxylation phenomena, i.e. condensation of external silanol groups with the release of water molecules and formation of strained siloxane bridges. The TGA results evidenced

that probably the thermal stability of the ether groups is slightly higher than that of the urea groups, with the HSO₃-NOS-F sample being more stable than HSO₃-NOS-H, from a thermal point of view. After investigating the amount and the stability of the organic species constituting the hybrid materials, the focus was shifted to the textural properties. N₂ physisorption analysis at 77 K was conducted on the two hybrid catalysts and on a pure silica sample obtained with the same synthetic methodology in order to study the specific surface area, the free pore volume of the materials and the effect of the presence of the R-Si(OR')₃ species in the synthesis mixture (Fig. 2, Table 1). The isotherms show a type IV behaviour (IUPAC), with a hysteresis loop typical of conventional mesoporous materials. The N₂ uptake is also compatible with mesoporous materials obtained through a F-catalysed solgel approach. Furthermore, cavitation and an ink-bottle pore shape could give rise to hysteresis and sharp peaks in the desorption band.¹² The Brunauer-Emmett-Teller (BET) method was used to obtain information regarding the surface area of the catalysts. Both organo-catalysts show a surface area comparable with that of the pure silica reference material (802 m² g⁻¹). Specifically, HSO₃-NOS-F exhibits an area of 816 m² g⁻¹ whereas HSO₃-NOS-H shows a surface area of 683 m^2 g⁻¹. This slightly lower value may be related to the usage of a bulkier organosilane precursor used in the one-pot synthesis of the solid. The adsorption branches of the isotherms were analysed by means of (i) NLDFT (non-localized density functional theory) and (ii) Barrett-Joyner-Halenda (BJH) methods to obtain information on the pore-size distributions. Both functionalized non-ordered silicas and the reference pure silica material show a pore distribution spacing between 20 and 60 Å with a peak centred at about 35 Å, typical for non-ordered silica materials obtained through a F-catalyzed sol-gel synthesis process.12 In all three samples a small amount of micropores is present. This was already observed in other syntheses carried out in NH4F medium.^{12,21} After exploring the amount and stability of the organic moieties and the textural properties of the hybrid catalysts, ss NMR and



Fig. 1 TGA and DTA curves of HSO_3 -NOS-H (a and a') and HSO_3 -NOS-F (b and b').



Fig. 2 A) N_2 adsorption/desorption isotherms at 77 K of HSO_3-NOS-H, HSO_3-NOS-F and non-ordered silica (NOS, reference material). B) Pore-size distribution of the materials in the mesopore range.

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estimated by means of the non-linear DFT method. V _{BJH} was calculated from the adsorption branch of the isotherms								
	SSA_{BET}	SSA_{DFT}	SA _{Micro}	SA _{meso}	$V_{\rm BJH}$	$V_{\rm DFT}$	V_{micro}	V_{meso}

Table 1 Textural properties of HSO₃-NOS-H and HSO₃-NOS-F. Microporous and mesoporous contributions to the surface area and pore volume were

	$\begin{array}{c} SSA_{BET} \\ \left(m^2 \ g^{-1}\right) \end{array}$	$\begin{array}{c} SSA_{\rm DFT} \\ \left(m^2 \ g^{-1}\right) \end{array}$	${{\rm SA}_{{ m Micro}} \over {\left({{m}^2 \ {g}^{ - 1}} ight)}}$	${{\rm SA}_{{ m meso}} \over {\left({{{\rm{m}}^2}\;{{\rm{g}}^{ - 1}}} ight)}}$	$V_{\rm BJH} \ ({\rm cm}^3 {\rm ~g}^{-1})$	$\left(\mathrm{cm}^{3} \mathrm{g}^{-1} \right)$	$V_{ m micro} \ (m cm^3 g^{-1})$	$V_{\rm meso}$ (cm ³ g ⁻¹)
HSO ₃ -NOS-H	683	549	91	458	0.39	0.485	0.0301	0.455
HSO ₃ -NOS-F	816	613	36	577	0.49	0.6	0.0163	0.584
NOS	802	607	80	527	0.52	0.643	0.027	0.616

FTIR spectroscopic characterization was carried out to study the organic-inorganic interaction and to assess the acidic properties of the hybrids.³⁰ Prior to recording the FTIR spectra, all the samples have been outgassed at 453 K for 2 h in order to remove physisorbed water. The HSO3-NOS-H spectrum (Fig. 3, curve c) appears quite different compared with the pure silica reference material, NOS (Fig. 3, curve a). The presence of the bulky silyl-derivative in the synthesis leads to a lower amount of isolated silanols in the final material: a signal centred at 3745 cm⁻¹, due to the O-H stretching mode of Si-OH groups, is visible but its intensity is much lower than that of the reference material. Instead, a broad signal related to silanols interacting with each other through a H-bond is visible between 3500 and 3200 cm⁻¹. A number of signals related to the stretching mode of C-H groups present in the aromatic ring, in the propyl linker and in eventual uncondensed alkoxy groups, are visible between 3000 and 2800 cm⁻¹. The low frequency region appears quite rich in signals, due to the presence of the urea group. The signal centred at 1685 cm⁻¹ is attributed to the stretching modes of the C=O bond of the urea group. The presence of the urea group is confirmed by the amide II band, centred at 1600 cm⁻¹, which is related to a motion combining the N-H bend-



Fig. 3 FTIR spectra of non-ordered silica (NOS, curve a), HSO₃-NOS-F (curve b) and HSO₃-NOS-H (curve c). The samples have been outgassed at 453 K prior to recording the spectra.

ing and C-N stretching of the amide group.³¹ Lastly the sharp band at 1535 cm⁻¹ is ascribed to the C-C stretching of the aromatic ring. In addition, a weak band at 1380 cm⁻¹ is visible due to the S=O asymmetric stretching mode of sulfonic groups. Shifting the focus to the HSO₃-NOS-F FTIR spectrum (Fig. 3, curve b), it can be observed that by using a less bulky silvl-derivative as an organosilane precursor, the amount of isolated silanols (3745 cm⁻¹) in the resulting material appears comparable to that of the pure silica one. A composed signal centred between 3000 and 2800 cm⁻¹ is observed and attributed to the stretching mode of C-H groups present in the propyl chains (and in uncondensed alkoxy groups). Due to the simpler liking point between the propyl chain and the aryl-sulfonic moieties, in this spectrum, the low frequency region appears poorer in signals, with a sharp band centred at 1500 cm⁻¹, related to the C-C stretching of the fluorinated aromatic ring. In order to study the acidity of the sulfonic groups exposed to the inorganic silica surface, CO was adsorbed at 80 K on the hybrid catalysts (Fig. S3[†]). Both materials behave equally upon interaction with CO. Focusing on the high frequency region, the signal related to the stretching modes of isolated silanols (3745 cm⁻¹) is shifted downward, forming a broad signal centred at approximately 3644 cm⁻¹. The 100 cm⁻¹ frequency shift is consistent with previous studies reported on purely siliceous materials.²⁸ In the CO stretching region, at low coverages a signal centred at 2155 cm⁻¹ arose, due to the CO molecules interacting with the SiOH groups on the surface of the support.²⁸ At higher CO dosages the typical band related to the stretching mode of the free CO molecule appears (v_{CO} liquid-like at 2138 cm⁻¹).³² Given a specific site with which CO is interacting, the blue shift of the stretching mode is expected to be proportional to the ability of the site to accept electronic density, i.e. its acidity. Nevertheless, despite the presence of highly acidic sulfonic groups, no signal is observed at higher frequencies other than that of CO interacting with silanols. The CO adsorption at 80 K is able to reveal only mild acidity due to the available Si-OH of the inorganic support. The high concentration of external silanol groups masks the presence of sulfonic groups present in the hybrid materials. Then, a more selective probe molecule has been used, such as ammonia. NH₃ was adsorbed at room temperature on the hybrids and on the pure non-ordered silica support (Fig. 4). NH₃ interaction with NOS (Fig. 4A) produced typical features due to the formation of a H-bond between Si-OH groups of the silica and the probe molecule.³³ At high NH₃ pressure (30 mbar), bands at 3400 and 3320 cm⁻¹ appear, overlapped with a



Fig. 4 FTIR spectra of NH₃ adsorption at 298 K on NOS (A), HSO₃-NOS-H (B), and HSO₃-NOS-F (C). Red curves: Hybrids under vacuum before NH₃ adsorption, black curves: adsorption of NH₃ at high pressure (30 mbar), blue curves: NH₃ outgassing at rt. B and C insets: FTIR difference spectra.

broader band centred at 3020 cm⁻¹ while the band at 3745 cm⁻¹, due to the O-H stretching mode of free silanols (red curve), almost completely disappears (bold black curve). The broad band centred at 3020 cm⁻¹ is assigned to the O-H stretching of the silanol groups H-bonded to NH₃ molecules. The bands at 3400 and 3320 cm⁻¹ are respectively due to the N-H asymmetric and symmetric stretching modes of NH₃ bonded to silanols. At lower frequency, a band at 1635 cm⁻¹ is also present which is assigned to the asymmetric bending mode of the ammonia molecules adsorbed on Si-OH groups. Such complexes are very weakly held as demonstrated by the fact that all their spectroscopic features progressively fade away when decreasing the NH₃ pressure and almost completely disappear upon outgassing the sample at room temperature for 30 minutes (blue curve), giving a spectrum which is similar to that of the bare NOS sample before NH₃ adsorption (red curve). Different from the behaviour observed upon NH₃ adsorption of the pure silica mesoporous support, the ammonia adsorption on both HSO₃-NOS-H (Fig. 4B) and HSO₃-NOS-F (Fig. 4C) hybrids produced, in the low frequency

region, bands at 1465 and 1485 cm⁻¹ due to the asymmetric bending mode of NH_4^+ protonated species, meaning that sulfonic acid groups are strong enough to protonate ammonia.³⁴ Ammonia protonation is an irreversible process; in fact upon NH_3 desorption at room temperature, the signal due to NH_4^+ ions is still visible on both hybrid catalysts (blue curves). In the insets are reported the difference FTIR spectra in order to better evidence the formation of the NH_4^+ bands that are partially overlapped with other signals typical of the organic part of the hybrids.

A series of multi-nuclear magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopic experiments have been conducted to study the hybrid organic-inorganic mesoporous silica-based catalysts. The successful incorporation of aryl-sulfonic acids in non-ordered mesoporous silica was established by ²⁹Si NMR spectroscopy while the integrity of the organic components on the hybrid catalysts was determined by ¹³C NMR spectroscopy. This information gave a first idea on local arrangements of organosilane species and furthermore was supported by various ¹H MAS NMR methods which would help to determine the proton environments as well as the acidic nature of the catalysts. The ²⁹Si population distribution as well as the organosilane functionalization in different hybrid catalysts was studied by ²⁹Si CPMAS NMR. Fig. 5 (left panel) shows the ²⁹Si CPMAS NMR spectra of the hybrid catalysts, where both Q and T Si sites are present.³⁰ There are three different Q silicon sites, namely Q^4 (Si(OSi)₄) silicon sites (at around -110 ppm), Q³ (Si(OSi)₃OH) silicon sites (at around -100 ppm) and Q² (Si(OSi)₂(OH)₂) silicon sites (at around -90 ppm) seen in the hybrid catalysts originating from the non-ordered mesoporous silica support. On the other hand, the signals from T^3 (RSi(OSi)₃) silicon sites (at around -66 ppm) and T² (RSi(OSi)₂OH) silicon sites (at around -58 ppm) stemming from the organosilane groups confirm their successful silica surface functionalization.²¹



Fig. 5 ²⁹Si (left panel) and ¹³C (right panel) CPMAS NMR spectra of various hybrid catalysts recorded at a 10 kHz MAS rate. A CP contact time of 2 ms was employed for ²⁹Si CPMAS while for ¹³C CPMAS values of 4 ms and 20 ms were used for samples HSO₃-NOS-H (red curves) and HSO₃-NOS-F (black curves), respectively.

Similarly, Fig. 5 (right panel) shows the ¹³C CPMAS NMR spectra of the as-synthesized hybrid catalysts. The assignments of the spectral resonances are based on either ¹³C solution-state NMR or on software predicted computed spectra. In fact, the ¹³C CPMAS NMR spectra of the hybrid catalysts show the typical 13C signals associated with organosilane groups confirming the integrity of the synthesis process. On the other hand, the incomplete hydrolysis of alkoxy groups from the precursors is clearly evident through the presence of their peaks (at around 15, 50 and 59 ppm). The weak aromatic resonances (110 to 145 ppm) in the HSO₃-NOS-F catalyst are due to the fact that no protons are directly attached to the phenyl carbons as the intensity of ¹³C resonances depends on the proton-carbon dipolar interactions in a CPMAS experiment. In addition, the presence of unreacted 3-bromopropyl silane was also detected in this sample. The ¹H MAS and spin-echo NMR spectra of the hybrid catalysts, previously treated at 180 °C for 90 minutes under vacuum, recorded at a MAS rate of 15 kHz are shown in Fig. 6, left and right panel, respectively. Firstly, the intense resonance at 1.7 ppm is attributed to isolated silanols originating from the mesoporous silica support and the broad shoulder in the range 2-10 ppm is ascribed to hydrogen bonded silanols.35 However, contributions from water, amine protons and sulfonic acid protons also fall in this broad shoulder as they are in mutually exchangeable state. Exchangeable protons undergo different binding dynamics and form spatially structured clusters of variable sizes with chemical shift values determined by exchange between bound water, free water, isolated SiOH, hydrogen bonded SiOH and acidic/basic protons. The resulting ¹H chemical shift is the weighted shift of the compounds which are involved in the fast chemical exchange.36 Furthermore, proton resonance peaks associated with organosilanes are clearly detected at around 1 ppm for aliphatic components and at around 7.5 ppm for aromatic units. No aromatic protons were detected in the HSO₃-NOS-F catalyst as they are substituted by fluorine. The sharp resonance peaks in the range 3.2 to 3.6 ppm are attributed to the alkoxy groups from the unhydrolysed

precursors. It is important to note that peaks due to residual ammonium fluoride, used as a catalyst in the synthesis of non-ordered mesoporous silica, were detected at 6.6 ppm. Finally, the narrow low intensity resonance detected at 9.4 ppm in the HSO₃-NOS-F catalyst is attributed to sulfonic acid protons (Fig. 6, inset) not in exchange with other compounds. The acidity of the hybrid catalysts was determined by adsorbing a basic probe molecule that would be converted to a protonated species upon contact with acidic sulfonic protons. Ammonia was adsorbed on the hybrid catalysts that were previously treated at 180 °C under vacuum for 90 minutes. ¹H spin-echo NMR spectra were recorded after ammonia adsorption and are shown in Fig. 7. It is clearly evident that ammonium ions were formed after adsorption as the intensity of the 6.6 ppm peak has increased. Furthermore, a small decrease in the peak intensity of sulfonic acid protons is also observed in sample HSO₃-NOS-F. It is important to note that every single sulfonic acid proton would be converted into four equivalent ammonium ion protons upon adsorption. The presence of a 9.4 ppm peak in the spectrum after ammonia adsorption also confirms the fact that not all sulfonic acid protons are accessible to ammonia. On the other hand, a marked increase in the formation of ammonium ions in sample HSO3-NOS-H after ammonia adsorption is surprising as no free sulfonic acid protons were detected in the ¹H NMR spectrum of the parent sample. As has been pointed out earlier, the sulfonic acid protons are in exchangeable state (either with water or with silanols or both) in this sample, however, they can easily protonate a stronger base upon its presence. On the other hand, sulfonic acid proton signals can also be overlapped with other signals or the resonance can be broadened due to stronger dipolar interactions. In order to circumvent such issues, we have employed a different probe molecule to determine the acid strength on these hybrids. It is well established that the ³¹P MAS NMR chemical shift scale can be used to determine the acidic



Fig. 6 ¹H MAS (left panel) and 1H spin-echo (right panel) NMR spectra of various hybrid catalysts recorded at a 15 kHz MAS rate. An echo delay (tau) of 2 ms was used in the spin-echo experiment. The inset shows the zoomed spectra.



Fig. 7 $\,^{1}$ H spin-echo NMR spectra of various hybrid catalysts, before (black) and after (red) ammonia adsorption, recorded at a 15 kHz MAS rate and an echo delay (tau) of 2 ms.

strength of solid acids by adsorbing trimethylphosphine oxide (TMPO).³⁷ The larger the ³¹P NMR down-field shift of the adsorbed TMPO molecule, the higher the acidity of the material.^{37,38} Fig. 8A shows the room temperature ³¹P MAS NMR spectra of HSO3-NOS-H and HSO3-NOS-F after TMPO adsorption. Both samples exhibit an intense peak at 47 ppm, assigned to physisorbed TMPO molecules. Interestingly, the resonance peaks at 89 and 90 ppm in HSO3-NOS-H and HSO₃-NOS-F, respectively, confirm the very strong acidity displayed by these hybrids. A recent article has charted the acid strength of super acids using ³¹P MAS NMR spectroscopy and the largest chemical shift for TMPO was reported to be 93 ppm for a sulfonated polymer embedded in montmorillonite.39,40 Therefore, it can be concluded that the arylsulfonic acid-based catalysts presented in this work display acid strength similar to 100% H₂SO₄ (Fig. 8B) The higher ³¹P MAS NMR chemical shift for catalyst HSO3-NOS-F confirms the higher acidity of this hybrid catalyst. To summarize, solid-state NMR methods provided detailed information on the local structure of organosilanes and dynamics of sulfonic protons. The presence of acidity of the catalysts was evidenced, by protonation of ammonia upon adsorption, through a ¹H peak at 6.6 ppm as well as by TMPO adsorption and ³¹P peak observation at around 90 ppm. Moreover, the structural integrity of the organosilane units and the hybrid nature of the silica backbone were confirmed by ¹³C and ²⁹Si CPMAS NMR experiments, respectively. The solid-acid catalysts outlined in Scheme 1 (HSO₃-NOS-H and HSO₃-NOS-F) were evaluated in the acetal formation reaction between benzaldehyde and ethylene glycol as shown in Scheme 2. This reaction is of particular interest to synthetic organic chemists, as it is used to protect aldehydes and ketones, making them stable under basic reaction conditions, to facilitate subsequent reduction and oxidation transformations.^{41,42} Preliminary catalytic findings as outlined in Fig. 9 show promising catalytic trends in both reactivity and recyclability, demonstrating the potential of these type of heterogeneous catalysts. The anchored catalyst HSO3-NOS-F demonstrates a slightly higher stability, showing high quantitative yields and recyclability under the experimental reaction conditions, thereby proving the robustness of the anchoring strategy for creating hybrid heterogeneous catalysts. Catalyst HSO3-NOS-



Fig. 8 31 P MAS NMR spectra (A) of various hybrid catalysts recorded at room temperature and a MAS rate of 15 kHz. * denotes spinning sidebands. A graph (B) showing the acid strength *versus* 31 P MAS NMR chemical shifts of various super acids catalysts reported in the literature (see ref. 39).



Scheme 2 Catalytic reaction used to test the reactivity and recyclability of HSO_3 -NOS-H and HSO_3 -NOS-F catalysts.

H shows a slightly lower activity, under the same reaction conditions, probably due to its lower acidity. It is highly likely that the presence of fluorine atoms in the benzene ring of catalyst HSO₃-NOS-F makes it more electron-poor, inducing a higher degree of acidity in the sulfonic acid moiety, compared to the urea derivative present in catalyst HSO₃-NOS-H.

We also investigated the scope of the acetalization reaction with different aldehydes and ketones using catalyst HSO₃-NOS-H to evaluate the wider potential of this anchored catalyst containing pendant acid sites (Table 2). Promising results were obtained when cyclohexanone and other electron-poor benzaldehydes were employed as substrates. As expected, electron-rich aldehydes represent a challenge due to their electronic nature and require longer reaction times or harsher reaction conditions. To evaluate wider industrial applicability, we also probed the effectiveness of this anchored catalyst in the transacetalization reaction achieving promising results when dimethoxy propane was used (60% yield).

Experimental

Synthesis of the materials

Synthesis of 2. Compound 1 was achieved by reacting sulfanilic acid (99%, Aldrich) with 1 equivalent of NaOH, in H_2O . 1 was reacted with 3-(triethoxysilyl)propyl isocyanate (95%, Aldrich) in acetonitrile, at 65 °C, under N_2 , overnight. The solvent was then evaporated under vacuum.

Synthesis of 3. A solution of 2, tetramethyl orthosilicate (98%, Aldrich), MeOH and H₂O was prepared and stirred until complete dissolution (solution A). A solution of NH_4F (Aldrich, 98%) in H₂O was prepared (solution B). Solution B was added to solution A and stirred at room temperature until gelation occurred. The gel obtained was aged at 36 °C for 24 h. Afterwards, the solid was dried overnight at 65 °C, ground



Fig. 9 Yields obtained with HSO_3 -NOS-H and HSO_3 -NOS-F catalysts in the acetalization reaction.

Table 2 Evaluating the wider scope of the anchored catalyst, ${\sf HSO}_{3}\text{-}{\sf NOS-H},$ for acetalization and transacetalization reactions

General reaction

CHO R +	R'_OH	
Aldehyde/ketone	Alcohol	Yield%
СПО СНО	ноон	56
$R = NO_2$	НОСОН	100
R = OMe	НО	10
0	ностон	100
Me Me	НООН	60
$R = NO_2$	CH ₃ OH	16

and washed with ethanol and H_2O . The final composition of the synthesis gel was as follows: $0.97TMOS: 0.03RSi(OR')_3:$ 4MeOH: $4H_2O: 0.00313NH_4F$.

Synthesis of 4. The material was obtained using the same procedure as the synthesis of 3, using (3-bromopropyl)-trimethoxysilane (97%, Fluorochem) instead of using compound 2.

Synthesis of 6. A solution of 5 (sodium 2,3,5,6-tetrafluoro-4-hydroxybenzenesulfonate, 98%, TCI Europe) in DMSO was prepared under N₂. DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, 97.5%, Aldrich) was added and the mixture was stirred for 10 minutes. Br-Propyl functionalized silica (4) was added and the mixture was stirred at 100 °C for 16 h. Afterwards the suspension was cooled down at room temperature and the solid was filtered and washed abundantly with H₂O and ethanol.

Synthesis of HSO₃-NOS-H and HSO₃-NOS-F. The supported sodium sulfonates 3 and 6 were exchanged three times with a 0.05 M HCl solution in EtOH at room temperature.

Catalytic test

The anchored, solid-acid catalysts, HSO_3 -NOS-H and HSO_3 -NOS-F (4 mol%), were added into a glass-lined reactor, equipped with a Dean Stark apparatus and a condenser, followed by subsequent addition of the aldehyde (1 equiv., 0.5 mmol), dialcohol (30 equiv.) and toluene (5 ml). The reaction mixture was stirred at 120 °C for 20 h and the yield was quantified by ¹H-NMR using an internal standard. Recycling: the crude reaction was filtered, and the catalyst was washed with dichloromethane, dried under vacuum and reused in the next reaction.

Characterization

¹H and ¹³C NMR spectra were recorded on a Bruker 300 spectrometer and the chemical shifts are reported in ppm rel-

ative to residual proton solvent signals. Nitrogen adsorption isotherms were measured at 77 K with a Micromeritics ASAP 2010 volumetric adsorption analyser. Before the measurement, the sample was outgassed for 12 hours at 80 °C. The BET specific surface area was calculated from the nitrogen adsorption data in the relative pressure range from 0.04 to 0.2. The total pore volume was obtained from the amount of N₂ adsorbed at a relative pressure of about 0.99. The pore diameter and the pore size distribution were obtained using the Barrett-Joyner-Halenda (BJH) method on the adsorption branch of the isotherms. The adsorption branch of the N₂ physisorption isotherm was analysed by means of the NLDFT (nonlocal density functional theory) method, to obtain the pore size distribution of the materials. Thermogravimetric analyses (TGA/DTA) of materials were performed under argon flow (100 mL min⁻¹) with a SETSYS Evolution TGA-DTA/DSC thermobalance, heating from 40 to 1000 °C at 5 °C min⁻¹. The FTIR spectra of self-supporting pellets were collected under vacuum conditions (residual pressure $<10^{-5}$ mbar) using a Bruker Equinox 55 spectrometer equipped with a pyroelectric detector (DTGS type) with a resolution of 4 cm^{-1} . CO was adsorbed at 77 K and NH₃ was adsorbed at room temperature using specially designed cells permanently connected to a vacuum line to perform adsorption-desorption in situ measurements. The FTIR spectra were normalized with respect the pellet weight and, whenever specified, are reported in difference-mode by subtracting the spectrum of the sample under vacuum from the spectrum of the adsorbed molecules. Solid-state NMR spectra were acquired on a Bruker Advance III 500 spectrometer and a wide bore 11.7 Tesla magnet with operational frequencies for ¹H, ¹³C, ³¹P and ²⁹Si of 500.13, 125.77, 202.47 and 99.35 MHz, respectively. A 4 mm triple resonance probe with MAS was employed in all the experiments. The samples were packed on a zirconia rotor and spun at a MAS rate between 10 and 15 kHz. The magnitude of radio frequency (RF) fields was 100 and 42 kHz for ¹H and ²⁹Si, respectively. The relaxation delay between accumulations was 2 and 2.5 s. For ¹³C and ²⁹Si cross polarization (CP) MAS experiments, RF fields of 55 and 28 kHz were used for initial proton excitation and decoupling, respectively. During the CP period the ¹H RF field was ramped using 100 increments, whereas the 13C/29Si RF fields were maintained at a constant level. During the acquisition, the protons are decoupled from the carbon atoms/silicon atoms by using a two-pulse phase-modulated (TPPM) decoupling scheme. A moderate ramped RF field of 62 kHz was used for spin locking, while the carbon/silicon RF field was matched to obtain the optimal signal. A rotor-synchronised spin-echo sequence $(\pi/2-\tau-\pi-\tau-acquisition)$ was also applied to record the ¹H NMR spectra with a delay time τ of 2 ms. The delay time was chosen as an optimised compromise between the signal decay owing to relaxation and the resolution gain owing to longer delay times. ³¹P MAS NMR spectra were recorded using high power proton decoupling and the RF field for the 90 degree pulse was 83 kHz. All chemical shifts are reported using the δ scale and are externally referenced

to tetramethylsilane (TMS) at 0 ppm for 1 H, 13 C and 29 Si. Ammonium dihydrogen phosphate (1 ppm) was used as a standard for the 31 P nucleus.

Prior to the adsorption of TMPO probe molecules, the catalysts were packed onto a 4 mm zirconia rotor and evacuated at 180 °C for 90 minutes in a high vacuum line. After that, TMPO dissolved in anhydrous dichloromethane was added to the rotor and rapidly closed with a cap and left for adsorption for one hour. Later, the rotor was opened and attached back to the high vacuum line for the complete removal of dichloromethane at room temperature. Subsequently, the rotor was closed with a zirconia cap and heated to 160 °C for 30 minutes followed by submission to NMR spectral recording.

Conclusions

In this work, two novel organosiliceous hybrid catalysts containing sulfonic acids were successfully synthesized through a multi-step approach. One of them, namely HSO₃-NOS-H, contains aryl-sulfonic groups, while the other, HSO₃-NOS-F, has aryl-sulfonic groups in which the aromatic ring is fluorinated. The textural properties of the materials showed characteristics typical of mesoporous materials, with a BET surface area of about 600–700 $m^2 g^{-1}$ and a narrow pore size distribution centred at about 35 Å, which is particularly notable considering that the co-condensation of TMOS and silylderivatives was carried out in the absence of templating agents. Moreover, the successful incorporation of organic functionalities opens up the possibility of designing porous catalysts for specific substrates of different sizes and functionalities, as by simply changing the gel composition, the textural properties (specifically, pore size) can be tuned.^{7,12} FTIR spectroscopy, together with ¹H, ¹³C and ²⁹Si solid state MAS NMR, was implemented to study the integrity of the organic moieties and the speciation of the silicon atoms within the hybrid materials. The adsorption of a strong base such as ammonia as a probe molecule followed by FTIR and ¹H spinecho NMR spectroscopy has allowed the acidic behaviour of the two types of sulfonic acids to be studied, highlighting that the hybrid with fluorinated aryl-sulfonic groups has a greater availability of the acid sites. On the other hand, ³¹P MAS NMR data on the TMPO adsorbing hybrid catalysts revealed the super acidic nature of the materials. Preliminary catalytic results indicate the superior performance and recyclability of the HSO₃-NOS-F catalyst, compared to the HSO₃-NOS-H analogue, highlighting the effectiveness of the anchoring strategy. The acidic nature of the organosiliceous hybrids can be suitably modulated to influence the catalytic properties of the materials and the wider potential of these anchored catalysts in transacetalization reactions expands the scope of their industrial applicability. By capitalizing on the structure-property links, derived from the design methodology and associated characterization, we can devise catalytic applications that prove the merits of solid-acid centres on hybrid heterogeneous catalysts.

Conflicts of interest

There are no conflicts to declare.

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