CF$_3$SO$_3$H and CF$_3$SO$_3$H/CD$_3$CN adducts in silicalite channels as model systems for H-ZSM-5 Brønsted acidity evaluation

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The vibrational properties of triflic acid and of triflic acid–acetonitrile adducts adsorbed in silicalite channels are described. The spectroscopic modifications induced on triflic acid by the acid–base interaction are compared with those of the HCl/acetonitrile adducts formed *in situ* in the silicalite channels, and with those of the H-ZSM-5/acetonitrile and of the H-Nafion/acetonitrile systems. It is concluded that triflic acid in silicalite shows an acidity almost comparable to that of H-ZSM-5 and of H-Nafion.

1. Introduction

Triflic acid is widely known for its superacidic properties and in the seventies it was used in the form of the CF$_3$SO$_3$H–SbF$_5$ complex supported on Al$_2$O$_3$ as a solid superacid catalyst for isomerization and alkylation reactions of alkanes [1]. More recently, Topsøe et al. [2,3] have patented a catalyst for isobutane/alkene alkylation composed by triflic acid supported on silica gel. The use of zeolites H-Y as triflic acid supports gave results in the synthesis of MTBE [4], even if it was lately shown that the catalytic activity was more related to the formation of extra-lattice Al in the zeolite rather than to the direct presence of triflic acid [5]. Despite these interesting catalytic potentialities, the number of studies about the characterization of these systems is almost nothing [6]. The complete lack of information is particularly negative in the case of zeolites, because the characterization of the acid properties of triflic acid encaged in zeolitic frameworks would be also interesting for modelization purposes. In fact, the comparison of the spectroscopic properties of triflic acid/base adducts formed *in situ* in silicalite channels with those of the Brønsted sites/acetonitrile adducts in H-ZSM-5 could afford a simple way to evaluate the acid strength of H-ZSM-5 and other similar zeolites with low Al content. The utility of this method has been already shown in a previous study on the HCl–silicalite system [7,8], where it has been shown that the "effective" acid strength of the structural Brønsted groups of H-ZSM-5, H-mordenite and H-Beta is much higher than that of HCl entrapped in silicalite and that does not only depend on the local structure of the Brønsted groups, but also, although to a smaller extent, upon the tridimensional structure of the zeolite. However, due to its low acid strength, the HCl molecule entrapped in the channels of a purely siliceous MFI structure is not the ideal candidate for the simulation of the

strong acid Si(OH)Al zeolitic groups. In contrast, this is not true for triflic acid, whose acid strength (Hammet function $H_0 = -14.6$) [9] is presumably nearer to that of the Brønsted sites of H-ZSM-5, H-mordenite and H-Beta. On this basis, following the same method already verified for the HCl–B (B = base) adducts formed in the silicalite, we have decided to study the spectroscopic properties of triflic acid and of triflic acid–acetonitrile adducts synthesized *in situ* in the silicalite channels. The acid strengths of triflic acid adsorbed in the channels of the purely siliceous MFI structure and the acid strength of constitutional Brønsted sites of H-ZSM-5 and H-Nafion [10] are then compared.

2. Experimental

The silicalite sample (kindly supplied by ENICHEM laboratories, Novara, Italy) was synthesized in a Na, K, Al, Fe-free form (<20 ppm) following the procedure described in [11,12], where also details about its characterization are reported. Before adsorption the silicalite sample was activated at 973 K for 2 h. The thermal treatments (under high vacuum) and the spectroscopic measurements have been performed on samples in the form of self-supporting wafers. H-Nafion film was obtained by evaporation of a concentrated solution of Nafion EW 1100 in aliphatic alcohols/water mixture (from Aldrich). To obtain fully dehydrated samples, the polymer film was outgassed at 383 K under vacuum for 1 h.

CF$_3$SO$_3$H and CD$_3$CN were high-purity Aldrich products and were dosed from the gas phase. Proton exchange between methyl and sulfonic groups has been observed in limited amounts.

The IR measurements were performed at RT at 2 cm^{-1} resolution on a Bruker 66 instrument equipped with a MCT cryogenic detector.
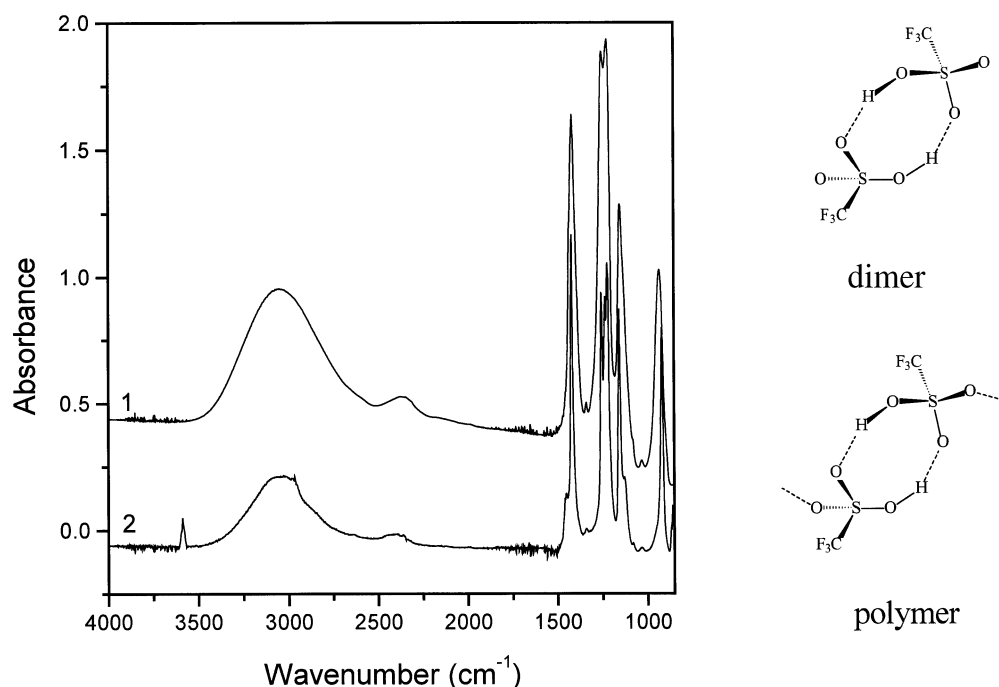
Figure 1. IR spectra of liquid (curve (1)) and gas-phase (curve (2)) triflic acid at $T = 298$ K.

3. Results and discussion

3.1. Adsorption of triflic acid on silicalite

In order to facilitate the description of the interaction between triflic acid and silicalite, it is useful to briefly recall the fundamental spectral features of triflic acid (in liquid and in gas phase). The spectra of pure liquid triflic acid (figure 1, curve (1)) show a broad absorption centered at 3050 cm^{-1} (HWFM = 500 cm^{-1}) and a less intense satellite at 2300 cm^{-1}, extending up to 1500 cm^{-1}. This complex absorption is due to the ν(OH) stretching mode of $(CF_3SO_3H)_n$ ($n \geqslant 2$) oligomers (see scheme in figure 1).

The satellite at 2300 cm^{-1} is an overtone of a $\nu_{sym}(SO_2)$ mode at about 1150 cm^{-1}, enhanced by a Fermi resonance effect with the ν(OH) mode. When the spectrum of the gas is considered (figure 1, curve (2)), we note that besides the bands characteristic of the presence of hydrogen-bonded oligomers (in this case dimers) [13], a band at 3588 cm^{-1} is also present, due to the ν(OH) stretching mode of the monomer molecule deriving from the monomer–dimer equilibrium in gas phase. Its weak intensity is clearly indicative of a strong tendency of triflic acid molecules to form hydrogen bonds even in the gas phase. The peaks associated with CF_3 groups are at 569 cm^{-1} ($\delta_{as}(CF_3)$), 771 cm^{-1} ($\delta_{sym}(CF_3)$) and 1150–1280 cm^{-1} (ν_s, $\nu_{as}(CF_3)$), while those mainly associated with the SO_2 groups are at 1440–1400 cm^{-1} (broad band in the liquid phase, narrow band at 1421 cm^{-1} in the gas phase; ν_{as}, $\nu_s(SO_2)$), 1150–1280 cm^{-1} ($\nu_s(SO_2)$) and 621 cm^{-1} (δ(OSO)). Finally, the modes involving the S–OH groups are at 1122 cm^{-1} (δ(SOH)), 496 cm^{-1} (wag(SOH)) and 930 cm^{-1} (ν(S–OH)) [14,15].

It must be recalled that not only the ν(S–OH), but also all bands due to ν(SO) modes are highly sensitive to the deprotonation of the acid, since the loss of the proton causes the delocalization of the negative charge among all the S–O bonds in the SO_3^- moiety with subsequent variation of the force constants. For this reason the bands at about 1400 and at 930 cm^{-1} can be used to determine the degree of dissociation of the acid [16].

Coming to the triflic acid/silicalite interaction (figure 2), the following can be commented:

(i) The IR spectrum of silicalite outgassed at 700 °C shows the characteristic peak at 3745 cm^{-1} due to the ν(OH) stretching of isolated silanols [11,12].

(ii) Upon adsorption of increasing doses of CF_3SO_3H, the intensity of the peak at 3745 cm^{-1} gradually decreases, while, at the same time, a very broad and composite absorption between 3600 and 1500 cm^{-1} develops (with components at 3620, 3420, 3170, 2900, 2673 and 2300 cm^{-1}). At the highest pressures (spectra not shown) the peak at 3745 cm^{-1} is not present anymore. A clear isosbestic point also appears at about 3650 cm^{-1}, showing that a correlation between the two observed phenomena exists.

(iii) A complex absorption in the 1360–1450 cm^{-1} interval composed of at least three overlapping components (at 1434, 1424 and 1411 cm^{-1}) develops as the pressure of the gas increases.

The gradual erosion of the 3745 cm^{-1} peak and the formation of the broad and complex absorption in the 3600–1500 cm^{-1} range is mainly associated with the formation of hydrogen-bonded species as shown in scheme in figure 2. In particular, the components below 3000 cm^{-1}
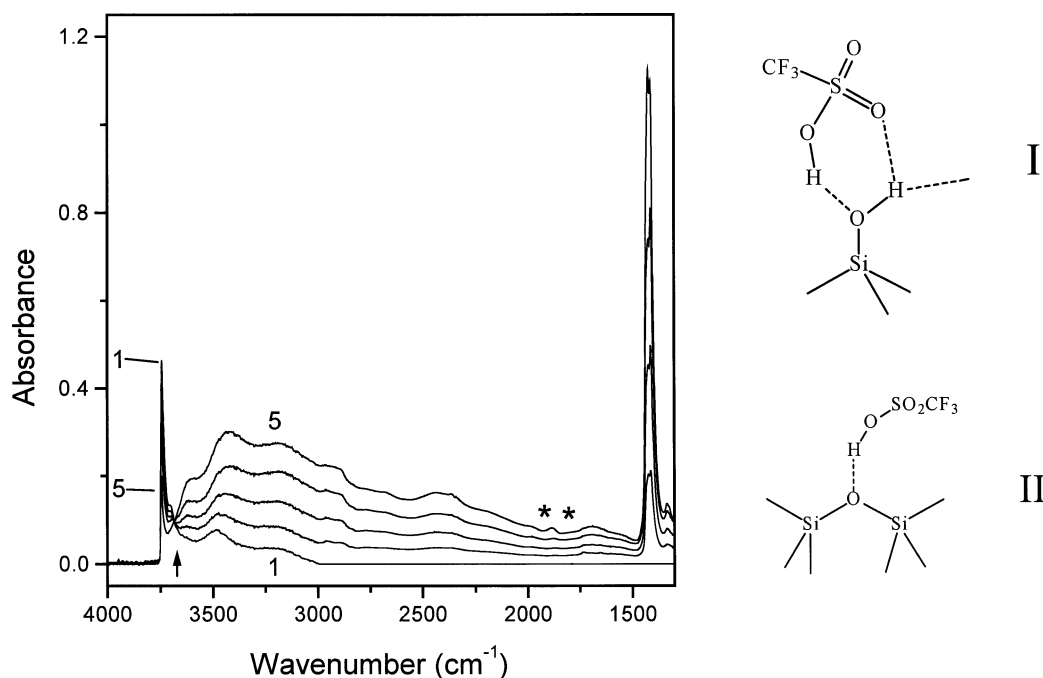
Figure 2. IR spectra of increasing doses of triflic acid on silicalite (outgassed in high vacuum at 973 K) at $T = 298$ K. Spectra have been plotted following the procedure described in [21].

can be attributed to combination modes, enhanced by Fermi resonance effects, of the perturbed $\nu(\text{OH})$ mode of $-\text{SO}_3\text{H}$ groups in structure I (figure 2) with low-frequency vibrations of the $-\text{SO}_3\text{H}$ group (i.e., the 2673 cm^{-1} band is given by 1420 cm^{-1} ($\nu_{\text{as}}(\text{SO}_2)$) + 1280 cm^{-1} ($\nu(\text{CF}_3)$ or $\nu_{\text{s}}(\text{SO}_2)$), the 2300 cm^{-1} band is due to the 2×1150 cm^{-1} ($\nu(\text{CF}_3)$ or $\nu(\text{SO}_2)$). The components in the 3650–3150 cm^{-1} range can be plausibly attributed to the $\nu(\text{OH})$ modes of silanols interacting with the SO groups (structure I) of triflic acid, and to $\nu(\text{OH})$ of triflic acid interacting with siloxane bridges (structure II in figure 2).

For sake of concision, we will not try a more detailed discussion of the IR spectrum of adsorbed triflic acid, because it is not relevant for the scope of the paper. Note how the preferential erosion of the low-frequency tail of the 3745 cm^{-1} peak upon triflic acid adsorption demonstrates that silanols in internal positions (responsible for the low-frequency tail of the silanol peak [11,12]) are involved.

3.2. The IR spectra of triflic acid–CD₃CN adducts synthesized in situ in the silicalite channels: comparison with H-ZSM-5 and H-Nafion adducts

The IR difference spectra of increasing doses of acetonitrile on a preadsorbed dose of triflic acid (corresponding to spectrum (5) of figure 2) are shown in figure 3. The interaction with CD₃CN leads to the consumption of the $(\text{CF}_3\text{SO}_3\text{H})_n$ complexes and to the formation of bands at about 2600 (A band), 2250 (B) and 1600 cm^{-1} (C) ($I_\text{B} > I_\text{A} > I_\text{C}$). The ABC triplet is characteristic of strongly hydrogen-bonded systems and is indicative of the formation of $\text{CF}_3\text{SO}_3\text{H}\cdots\text{NCCD}_3$ species. Acetonitrile also interacts with silanols and destroys preformed silanols–

triflic acid adducts (band at 3620 cm^{-1}) with formation of CD₃CN$\cdots$HOSi species (band at about 3375 cm^{-1}) [7]. The structure of the ABC triplet is similar to that observed for the acetonitrile/H-ZSM-5 and for the acetonitrile/H-Nafion systems. Its baricenter, calculated following [17], is at 2417 ± 50 cm^{-1}, corresponding to a shift $\Delta\nu(\text{OH}) = -1170 \pm 50$ cm^{-1}. This difference has been calculated with respect to the $\nu(\text{OH})$ frequency of the acid molecule in the gas phase at 3588 cm^{-1}; this is a small approximation, as the real difference should be calculated with respect to the monomer frequency, in an environment having a value of dielectric constant of 1.6 (*vide infra*).

The normalized value of $\Delta\bar{\nu}/\bar{\nu}$ for the CF₃SO₃H–NCCD₃ adduct can be compared with the $\Delta\bar{\nu}/\bar{\nu}$ figure of the SiOH$\cdots$NCCD₃ adduct in a Bellamy–Hallam–Williams plot [18,19], in which also all the known results obtained for hydrogen-bonded adducts formed in H-ZSM-5 (adducts between the Brønsted groups and various bases of proton affinity comprised in the 118–204 kJ/mol interval [19]) are included: figure 4 is then obtained. In the same figure, the data concerning the CD₃CN/H-Nafion and B–HCl adducts in silicalite are also reported (B = benzene, CD₃CN, THF, methyl and ethyl ether) [8]. It can be noticed that the data of H-ZSM-5 follow a linear relation for basic molecules with PA < 188.6 kcal/mol (i.e., the PA of acetonitrile). The slope of the line is related to the acid strength of the Brønsted sites by the empirical Paukshtis equation [20].

From figure 4 it is emerging that the acid strength of the Brønsted sites of H-ZSM-5 is very similar to that of triflic acid surrounded by the *same siliceous framework*. The acid
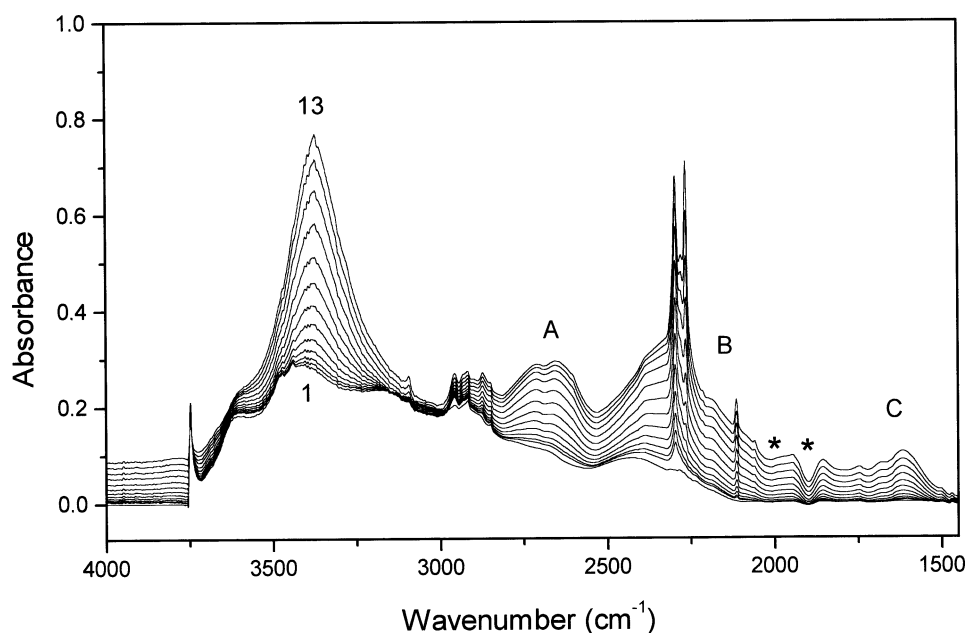
Figure 3. IR spectra of increasing doses of CD_3CN on CF_3SO_3H preadsorbed on silicalite at $T = 298$ K. Spectra have been plotted following the procedure described in [21]. ($*$) False bands associated with the shift of the skeletal modes induced by the filling of the channels with adsorbates [21].
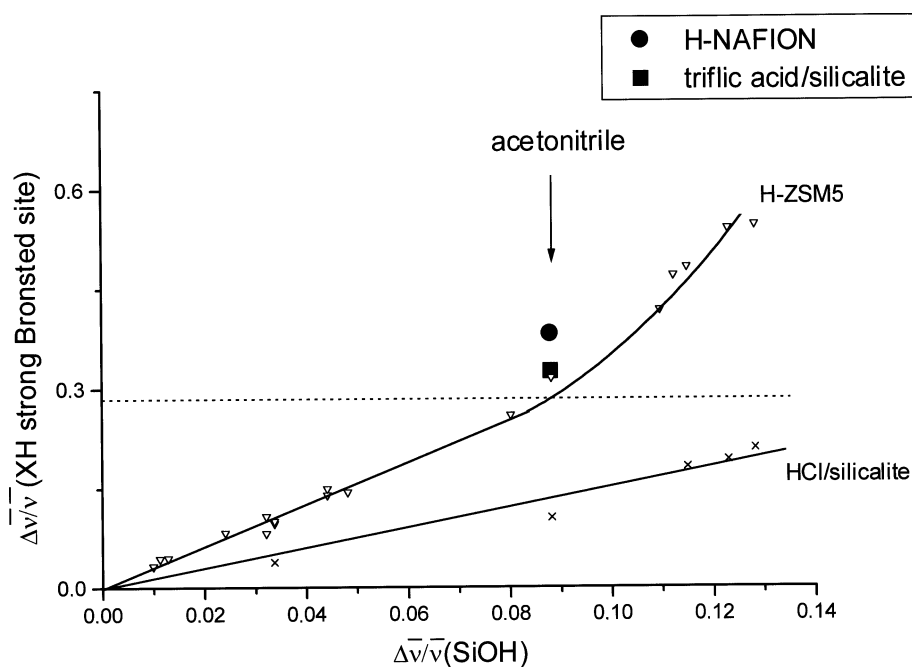

Figure 4. BHW plot [18] of the normalized shifts ($\Delta\bar{\nu}/\bar{\nu}$) of the ν(X–H) frequencies in X–H⋯B hydrogen-bonded complexes with different bases B versus the normalized shifts ($\Delta\bar{\nu}/\bar{\nu}$) of SiOH groups in hydrogen-bonded complexes with the same bases. XH are H-ZSM-5 [19], HCl in silicalite [8], CF_3SO_3H in silicalite and H-Nafion. Bases B are those used in [8,19]. The horizontal broken line separates the regions where the BHW plot is holding weak–medium strength hydrogen bonds from the region where a deviation is observed (strong hydrogen bonds characterized by a single flat potential energy minimum) [19]. It can be seen that the CD_3CN–CF_3SO_3H system is border-line.

proton in H-ZSM-5 is present in a non-polar environment, the relative dielectric constant of a zeolite lattice typically being 1.6 [22], so that the dissociation of an OH bond is inhibited. The comparison of the spectroscopic properties of the identical adducts in the same solid "solvent" guarantees that the adopted procedure is not affecting the spectroscopic results. Note that the interaction with H-Nafion seems to be slightly stronger. However, in this case the comparison is less straightforward since the "solvent" (Nafion membrane) is different.

The analysis of the bands due to the CN stretching mode (in the 2350–2250 cm⁻¹ range) is particularly useful to shed further light on this point, since it is known that the interaction with an acid site causes an upward
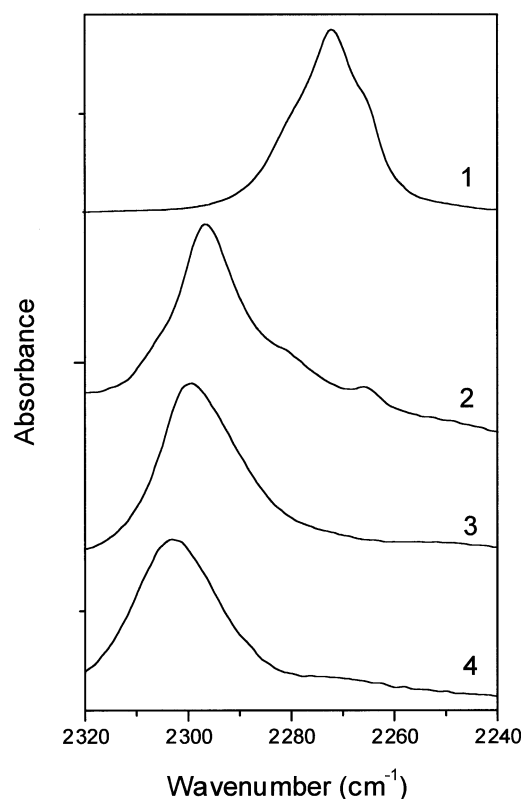
Figure 5. $\nu(CN)$ stretching mode region: comparison of the interaction between CD$_3$CN and (1) HCl in silicalite, (2) triflic acid in silicalite, (3) H-ZSM-5, (4) H-Nafion.

shift of the $\nu(CN)$ frequency (with respect to the gas phase) whose entity is correlated with the strength of the site [7]. In figure 5, a comparison of the interaction between HCl/CD$_3$CN in silicalite, triflic acid/CD$_3$CN in silicalite, H-ZSM-5/CD$_3$CN and H-Nafion/CD$_3$CN systems is reported. From this figure, it is clearly evident that on passing from adducts with HCl ($\overline{\nu}(CN) = 2270$ cm^{-1}), with triflic acid ($\overline{\nu}(CN) = 2297$ cm^{-1}), with H-ZSM-5 ($\overline{\nu}(CN) = 2300$ cm^{-1}), with H-Nafion ($\overline{\nu}(CN) = 2303$ cm^{-1}), the $\overline{\nu}(CN)$ frequency is increasing (even if the difference between triflic acid, H-ZSM-5 and H-Nafion is not very remarkable), so confirming the results obtained from figure 4.

4. Conclusions

The IR properties of triflic acid and of triflic acid–acetonitrile adducts synthesized *in situ* in the silicalite channels have been investigated. Triflic acid is adsorbed in the silicalite channels with formation of dimer and oligomers. An interaction with the silanols is also observed.

The comparison of the spectroscopic properties of the CF$_3$SO$_3$H–NCCD$_3$ in silicalite with the similar adducts formed with other acidic systems (HCl in silicalite, H-ZSM-5, H-Nafion) leads to the conclusion that triflic acid in silicalite shows an acidity almost comparable with that of H-ZSM-5 and of H-Nafion.

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