Synthesis and Characterisation of Mu-26 a Fluorinated All-Silica Zeolite with the STF Framework Topology: Evidence for a Triclinic Symmetry

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X-ray powder diffraction pattern analysis and multinuclear solid state NMR studies performed on the as-synthesised Mu-26 solid, a fluorinated all-silica zeolite with the STF framework topology, have revealed unambiguously a triclinic unit cell and space group P1 for this material.

One goal of many research groups working on microporous materials is the preparation of new microporous structures usable as catalysts for new applications.[1] Most of the novel silica based zeolite structures have been prepared from gel containing organic cations as structure-directing agents (SDAs) in alkaline media or more commonly in almost neutral fluoride-containing media.[2,3] The fluoride route may allow to obtain large single crystals[4] and consequently facilitates the structure determination by single-crystal X-ray diffraction. However, in some cases, the crystals are too small or systematically twinned. Zeolite SSZ-35[5] of framework topology STF,[6] represents a recent example of this fact. Its structure was first determined from synchrotron powder X-ray diffraction data collected on a calcined pure-silica sample prepared in an alkaline medium.[7,8] According to this first structural study, upon calcination, the unit cell of SSZ-35 seems to relax from a monoclinic (C2/m) to a triclinic symmetry (P-1). During the same period, Villaescusa *et al.* published the structure determined from low resolution powder X-ray diffraction data of calcinated ITQ-9,[9] a pure silica zeolite with the STF framework topology synthesized in the presence of fluoride anions and using racemic (R-,S-)N,N-dimethyl-6-azonia-1,3,3-trimethylbicyclo [3,2,1]-octane as the SDA. The unit cell volume is doubled compared to the one of calcinated SSZ-35 and the non-conventional space group I-1 was used.[9] Recently, the structure of as-synthesized ITQ-9 was determined from microcrystal X-ray diffraction data.[10] In this article, the authors described the structure in the centrosymmetric space group $P2_1/c$ with eight distinct crystallographic sites for the silicon atoms. Furthermore, the occluded SDA is disordered in the channels and at the end the reliability factors were rather high (RF(observed) $= 0.094$, wR(F^2 observed) $= 0.263$). Additionally, no ^{29}Si solid state NMR spectroscopy experiment was reported which could support the X-ray structure analysis.

We present here the synthesis and initial characterisations of the as-synthesized Mu-26 material, a pure silica zeolite with the STF framework topology also prepared via the fluoride route.

Many organic SDAs can be used to crystallize the STF-type zeolite.[11] For this study and to prevent the presence of a racemate within the zeolitic framework, we choose a new SDA, the cis-6,10-dimethyl-5-azonia-spiro[4.5]decane isomer which was converted to its hydroxide form. A general procedure for preparing the entitled material is as follow: 3.66 ml of tetraethylortosilicate (Aldrich, 98%) were hydrolysed in 3.465 g of an aqueous solution of the SDA (4.7 M) under stirring. After evaporation of the ethanol, the weight was adjusted to 3.87 g with water in order to obtain a molar ratio $H_2O/SiO_2 = 5$. Then, 0.41 ml HF (40% aq.) were added and the resulting thick paste was homogenised by hand stirring and then poured into a 20 ml Teflon-lined stainless steel autoclave. After 30 days of heating at 170 °C under static conditions, the resulting material was filtered, washed with water and dried at 60 °C for 12 hours.

Optical examinations of the crystallization product between crossed polars revealed that it was formed of elongated aggregates of interpenetrating crystals. Any attempts to separate them failed. Therefore the material was prepared for powder X-ray diffraction. The X-ray diffraction powder pattern of Mu-26 (Figure 1) contains well resolved peaks which show the evidence of a good crystallinity. To index this pattern, two programs, ITO19[12] and DICVOL91[13] trial and error indexing softwares, were used. Both methods gave the same solution. All the peaks were indexed with a triclinic unit cell where $a = 11.3176(6)$ Å, $b = 11.4321(6)$ Å, $c = 7.4145(4)$ Å, $\alpha = 96.425(5)^\circ$,

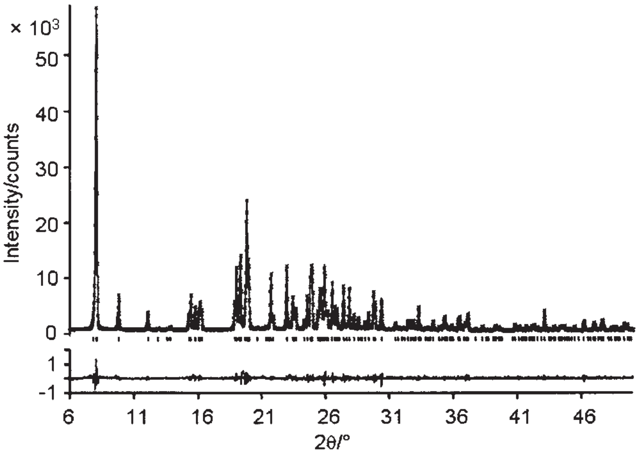

Figure 1. Profile fitting plot of Mu-26: experimental data (×), calculated profile (solid line) and difference (lower trace). The tick marks correspond to the positions of the allowed reflections. The XRD powder data were collected on a STOE STADI-P diffractometer with a linear 6° PSD in Debye-Scherrer geometry (Ge monochromator, $\lambda = 1.5406$ Å), step 0.02° 2θ, count time 45 s.

$\beta = 94.308(4)^\circ$, $\gamma = 104.631(5)^\circ$ and $V = 915.41(6)\,\text{Å}^3$. A careful examination of the low angle part of the X-ray powder pattern (i.e. $2 < 2\theta(^\circ) < 6$, not shown) collected slowly did not reveal the presence of any peaks which could suggest a doubling of the unit cell volume. It must be noted that these unit cell parameters are close to the ones of calcinated Mu-26 and SSZ-35[8] materials.

Also, the peak profile fitting performed on the X-ray powder pattern of Mu-26 (Figure 1) using the above unit cell parameters resulted in the good residual value $R = 0.034$ and strongly suggested that it is not necessary to double the unit cell volume.

^{1}H liquid NMR spectroscopy performed on the solution obtained by dissolution of the as-synthesised product in fluorohydric acid, proves that the organic SDA is intact within the zeolite framework.

The ^{19}F MAS NMR spectrum of Mu-26 (not shown) exhibits one asymmetric resonance at -79.2 ppm and a small amount of an impurity is detected. The simulation of the ^{19}F spinning sidebands patterns at different spinning frequencies gives an asymmetry parameter η_{cs} of 0.45 and a chemical shielding anisotropy δ_{cs} of -54.2 ppm. Such a chemical shielding anisotropy of the ^{19}F resonance indicates that F^- ions have a restricted mobility.[14] According to Koller et al.[14] this interaction may result from binding of the fluoride ion to one framework silicon atom, creating one pentacoordinated silicon atom.

The ^{29}Si MAS NMR spectrum is shown in Figure 2a. The spectral region extending from -102 to -118 ppm corresponds to tetrahedral ($Si(OSi)_4$) silicon sites.[15] The decomposition of this part of the spectrum, using the Winfit software,[16] gives 12 components (Figure 2b) with an area ratio of 1 : 1 : 3 : 1 : 1 : 1 : 1 : 1 : 1 : 2 : 1 : 1. The two signals observed at -148 and -145.8 ppm are in the spectral region corresponding to pentacoordinated silicon atoms.[17] They are due to $^1J_{\text{iso}}$ (^{29}Si, ^{19}F) coupling since the splitting of the resonance does not change with the magnetic field nor with the spinning frequency. The J-coupling constant determined from the line splitting is ±177 Hz. Moreover, the total area of both resonances is close to one, confirming that the observed signals account for one pentacoordinated silicon atom in agreement with the ^{19}F NMR result. Thus, the total number of non-equivalent crystallographic silicon sites is 16.

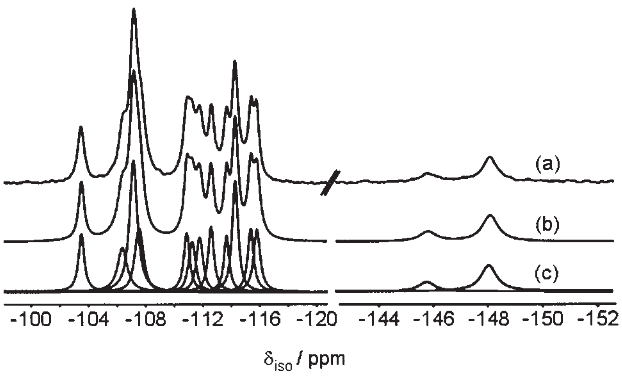

Figure 2. ^{29}Si MAS NMR spectra of Mu-26, (a) experimental, (b) simulated, (c) decomposition. Only the spectral region of isotropic resonances is shown. The proton decoupled MAS NMR spectra were recorded on a Bruker DSX 400 spectrometer with a spinning frequency of 4 kHz and a $\pi/2$ pulse duration of 5.4 μs. A recycle delay of 60 s was used. The ^{29}Si chemical shifts are referenced to TMS.

From the whole of the experimental results given above and in combination with the chemical and thermogravimetric analyses, the idealised chemical composition per unit cell of Mu-26 is $|C_{11}H_{22}NF|$ $[Si_{16}O_{32}]$. Therefore, the only possible space group for this structure is P1, which means a lower symmetry for the as-synthesized Mu-26 compared to the calcinated product. It is worthy to note that the calcinated Mu-26 product corresponds exactly to the calcinated SSZ-35 one.[8]

The preliminary structural investigations presented here revealed that as-synthesised Mu-26 is different from the corresponding SSZ-35 and ITQ-9 materials prepared in alkaline and fluoride media respectively.[7–9] Indeed, for the two last named, a monoclinic symmetry was proposed for both as-synthesized products with a unit cell volume twice the one of Mu-26 and eight non-equivalent crystallographic sites for the silicon atoms. Second harmonic generation measurements to confirm the non-centrosymmetric space group P1, full structure determination from molecular modelling combined with Rietveld refinement from high-resolution X-ray powder data and further ^{19}F/^{29}Si MAS NMR experiments are under progress and will be published elsewhere.

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