Structural changes in SAPO-34 due to hydrothermal treatment. A NMR, XRD, and DRIFTS study.

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Abstract

When SAPO-34 is used as an industrial MTO catalyst, structural transformations leading to permanent deactivation are inevitable. The performance loss is linked principally to a redistribution of Si in the material, leading to the formation of Si-islands/aggregates with a concomitant loss of Brønsted acidic sites and catalytic activity. In this work we have studied transformations taking place in a SAPO-34 sample after hydrothermal treatment by studying two samples with different levels of Si; 7 atomic % and 13 atomic % Si T-atoms, corresponding to about one and two Si per CHA cage respectively. The 13 % Si sample contains significant amount of silicon islands in its as-synthesized form, while the 7 % Si sample does not. The 7% Si sample was steamed for a week at 700 °C and a partial pressure of steam of 0.7 atm. The changes were analysed in the context of Si-island formation, and compared with the 13% Si sample. The results clearly illustrated existence of two distinct types of local aggregation of silicon: Silicon islands produced during synthesis and aggregate silicon reminiscent of silicon islands induced by hydrothermal treatment. The materials were synthesized with full ^{29}Si isotopic enrichment and allowed us, for the first time, to characterise the multiplicity of silicon species in great detail by ^{29}Si solid state NMR.

Keywords

1. Introduction

The microporous silicoaluminophosphate (SAPO) material SAPO-34 is topologically related to the Chabazite (CHA) zeolite and was first reported in 1984 by the Union Carbide Corporation[1]. SAPO-materials are composed of corner sharing TO_4 tetrahedra (T=Al, P) units where a partial substitution of P and/or Al atoms by Si has taken place. The structures are often related to zeolite frameworks. The main type of substitution mechanism for Si into a neutral $AlPO_4$ framework is exchange of a pentavalent P-atom by a tetravalent Si-atom, thereby forming a charge deficiency which is compensated by a positively charged structure directing agent (SDA) during synthesis or a monovalent cation after calcination. If this cation is a proton, a catalytically active material with Brønsted acidic sites is formed [1].

It has been found that when methanol reacts over the Brønsted acidic SAPO-34 at elevated temperatures, the selectivity to the two important polymer monomers ethene and propene, was high (the Methanol to Olefins, MTO, process). The origin of this high selectivity is a combination of high hydrothermal stability, three dimensional network with 8-ring channel size combined with large CHA cages, and moderate Brønsted acidity [2,3,4]. Recently, industrial plants for olefin production in China using coal as feedstock have been commisioned using the UOP/Hydro MTO process with an additonal UOP/Total olefin cracking process [4]. In addition to being a catalyst in the MTO process SAPO-34 materials are also used in e.g. deNOx reactions or as components in membranes for gas separation purposes [5,6].

A feature of the MTO process is the harsh hydrothermal conditions experienced by the catalyst both during conversion of methanol and, not least, during the removal of coke in the regeneration step. As a consequence, the catalyst becomes permanently deactivated after a number of cycles of reaction and regeneration [7]. From an industrial point of view, an important target is to understand, and hopefully improve, the long term stability of the SAPO-34 catalyst. The loss of performance is linked principally to a redistribution of Si in the material, leading to the formation of Si-islands (Si in the original material's framework) or Si-aggregates (extra framework Si) with a concomitant loss of Brønsted acidic sites and catalytic activity. Understanding of the mechanism of formation of such Si-islands/aggregates and their characteristics is therefore vitally

important. Recent work on shape and size, morphology and reaction mechanisms for desilication in SAPO-34 has shed more light on these issues [8,9,10,11], and Li et al. has studied stabilization of nano-sized SAPO-34 by hydrothermal treatments [12].

It is also important to control and understand Si-islands formed during synthesis since these might be relevant for the stability and performance, and extensive studies have been carried out on producing varying levels of Si incorporation in various SAPO materials. For SAPO-34 clustering of silicon into islands is expected to be significant when the total Si content approaches or goes beyond 6-8 T atomic % as this is approximately the theoretical value for having isolated Si atoms (i.e. no Si-O-Si linkages). However, the size, shape and mechanisms of formation in the as-prepared material are poorly understood. A rather early work by Sastre et al. describes stabilities of small Si-islands in terms of connectivities of the framework structure [13]. In general, the level of Si in the synthesis gel, the type and number of SDAs, and other synthesis conditions directs the Si-island formation. The relatively mild hydrothermal conditions during synthesis appear favourable for formation of Si-islands as a way to accommodate higher levels of Si into the framework.

A range of techniques have been applied to study the nature of Si-islands. Probably the best and most versatile method for mapping the local arrangement of T-atoms surrounding a Si atom is solid state NMR [14,15]. In zeolites and SAPOs, it is the local structure and the type of nearest neighbouring T atoms (either Si or Al) that mostly determines the Si chemical shift values. Any presence of structural defects, e.g. OH groups instead of AlO_4 tetrahedral units, or any major changes in T-O-T bond angles modify the picture somewhat [16]. Based on structural considerations, any given type of Si-island should give a unique Si peak- and intensity distribution in a ^{29}Si NMR spectrum. However, the likely existence of a distribution of different Si-island configurations and sizes complicates the analysis.

In the work we report here, we have studied a 7 atomic % Si sample (synthesized with almost exclusively isolated Si atoms and resembles a typical SAPO-34 catalyst) before and after steaming with the aim of contributing to a more detailed understanding of catalyst transformations that have taken place during the steaming. The sample was steamed for 7 days

(168h) at 700 °C and with a steam partial pressure of 0.7 atm. in order to form Si-islands/aggregates, with the aim of extracting new information on the structural transformations taking place under hydrothermal conditions. We assume that the steaming emulates the permanent deactivation that takes place during industrial use, but details would certainly be different. In our experience different steaming conditions like partial pressure of steam, temperature and time change details, but the data presented here represents the general outcomes from moderate steaming of SAPO-34 quite well. In order to facilitate detailed ^{29}Si NMR studies all samples were synthesized using a ^{29}Si source and we have compared the steamed sample with a high silica (13% Si) SAPO-34 sample where Si-islands were already formed during synthesis.

2. Experimental

2.1 Material synthesis

The starting point for synthesis of 100% ^{29}Si enriched SAPO-34 was the standard recipes based on the use of a silica sol (Ludox). The recipe was first modified by replacing the silica sol with a fine-particle silica source (fumed silica) with the normal isotopic abundance. Thereafter, the recipe was adapted for the relatively expensive 100% ^{29}Si silica source.

The SAPO-34 materials were synthesized using tetraethylammonium hydroxide (TEAOH) as the structure directing agent. Since one TEAOH molecule can be incorporated into the CHA cage of SAPO-34, providing one positive charge per cage, samples with up to 8.3 atomic % Si (T-atom precentage) in the framework contain isolated Si atoms [17].

The starting materials used were ^{29}SiO$_2$ (Isoflex, USA), pseudobohemite (72 % Al$_2$O$_3$ Catapal-B, Vista), orthophosphoric acid (85 %, Merck), and tetraethylammonium hydroxide (35 %, Sigma Aldrich). The samples were prepared in slightly different manners. Synthesis of the 7% Si SAPO-34 sample was based upon the procedure published in the patent by Mertens [18], which is a method that can be used for synthesizing both SAPO-18 and SAPO-34 materials by varying the Si content. At low Si contents SAPO-18 is formed. We used the initial reaction mixture: 0.25SiO$_2$: 1.0Al$_2$O$_3$: 1.0P$_2$O$_5$: 1.0TEAOH : 35H$_2$O. A mixture of orthophosphoric acid, TEAOH and deionized water was prepared and heated to 30 °C before ^{29}SiO$_2$ and Catapal-B were added under continuous stirring. After 2 hours of aging at 30 °C under stirring, the synthesis gel was sealed in a Teflon lined steel autoclave and heated to 165 °C with a heating rate of 5°C/h. The reaction mixture was kept at this temperature for 72 h with continuous rotation.

The 13 % Si SAPO-34 sample used the initial reaction mixture: 0.55SiO$_2$: 1.0Al$_2$O$_3$: 1.0P$_2$O$_5$: 1.0TEAOH : 50H$_2$O and prepared according to the patent by Sinkler et al. [19]. Here, the ^{29}SiO$_2$ was mixed well with TEAOH. In a separate beaker a mixture of orthophosphoric acid, deionized water and Catapal-B was prepared under vigorous stirring. The TEAOH solution was added to this mixture and stirred until obtaining a uniform gel. Finally, SAPO-34 seeds containing 11 % Si were added to the gel. Preparation of the 11% Si seeds is reported in Supporting Material. The amount of seeds used corresponds to 1 % of the total gel quantity. After thorough mixing the

synthesis gel was sealed in a Teflon lined steel autoclave and heated to 100 °C for 9 hours with continuous rotation. The temperature was then increased to 200 °C for an additional 48 h with rotation. Both reactions were stopped by quenching and the obtained powders were washed with deionized water before drying at 100 °C over night. Table 1 summarizes the synthesis conditons we have used.

Table 1. Summary of relevant synthesis parameters, including molar ratios in the reaction mixture, use of seeds, aging conditions, as well as synthesis temperature and time.

Sample	Molar ratio in reaction mixture					Seeds	Aging	Temperature	Time
	SiO_2	Al_2O_3	P_2O_5	TEAOH	H_2O				
7% Si SAPO-34	0.25	1	1	1	35	No	2 h at 30 °C	165 °C (5°C/h heating)	72 h
13% Si SAPO-34	0.55	1	1	1	50	Yes (11 % Si)	9 h at 100 °C	200 °C	48 h

The samples were calcined in slowly flowing air at 600 °C for 15 hours. Heating rate was 2 °C/min.

2.2 BET measurements.

Single point BET measurements were carried out using a Quantachrome Monosorb apparatus.

2.3 Steaming procedure

The steaming was carried out at 700 °C under a partial pressure of water of 0.7 atm, and a total pressure of about 1 atm. The sample was calcined as described above before steaming.

2.4 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS)

Scanning Electron Microscopy (SEM) images and EDS data were recorded on a FEI Nova NanoSEM 650 (FEI, USA) scanning electron microscope. The samples were deposited on a sample holder with adhesive carbon foil.

2.5 Powder X-ray diffraction (XRD)

Powder XRD data for the calcined and steamed 7 % Si samples were collected on a Bruker D8 Advance diffractometer in capillary mode with LynxEye XE detector and Leister LE mini heat gun. The data for the calcined 13% Si sample were collected on a Bruker D5000 diffractometer with Braun PSD in capillary mode with an Omega hot air blower. CuKα_1 radiation selected by a Ge (111) monochromator was used on both instruments. The samples were packed in 0.5 mm glass capillaries. The sample temperature was ramped to 250 °C prior to measurement and held at this temperature during data collection to ensure full dehydration of the framework. Data were collected from 7 to 80° 2θ. The unit cell dimensions of the calcined and steamed samples were determined by the Pawley method[20] using TOPAS [21]. Peak shapes were fitted using fundamental parameters and the background was fitted with a 7-term Chebyshev polynomial. All samples displayed some indication of a SAPO-34/18 intergrowth structure [22,23], however, the present study was limited to considering the SAPO-34 unit cell in the pattern fitting which allows easy comparison with literature data. A Stephens correction for peak anisotropy (trigonal, high symmetry form) was used in fitting the XRD data for the as-synthesized materials[24].

2.6 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

DRIFTS data were collecetd on a Bruker Vertex 70 FTIR-instrument equipped with a MCT-detector, together with a low temperature reaction chamber (CHC-CHA-3, Praying Mantis), and temperature controller (ATC-024-2, Harrick Instruments). Each spectrum is reported as the average of 128 scans at 2 cm^{-1} resolution. The sample was diluted in SiC and transferred to the sample cup before the pressure was lowered ($p < 3\times10^{-3}$ mbar). The samples were heated either at 200 °C (calcined 7% Si sample) or 360 °C (steamed 7% Si sample) under vacuum overnight, and thereafter cooled to approximately 30 °C before the temperature was lowered to approximately -150 °C by pouring liquid nitrogen into the Dewar connected to the reaction chamber. The temperature was measured with a T-element in contact with the sample inside the cell. Spectra

were collected for the pure sample when the temperature was stable. Thereafter, the sample was exposed to an increasing dose of CO and spectra were collected after each dosing. The spectra are reported in reflectance mode with the pure sample as background. The peak fitting was carried out assuming the bands to be described by a Gauss-function. The peak fitting routine of Origin 9 with a Levenberg Marquardt iteration algorithm was used. Due to the necessity of adding SiC to the SAPO-34 samples and the fact that we have small amounts of the steamed sample compared to the calcined samples, direct quantitative comparisons of areas in the different DRIFTS spectra are not possible.

2.7 Solid State Nuclear Magnetic Resonance Spectroscopy (SS NMR)

The NMR experiments were performed at 11.7 T (500 MHz proton resonance frequency) using a Bruker Avance III spectrometer equipped with a 3.2 mm triple resonance MAS probehead at room temperature. The MAS rate was 20 kHz for all experiments. Before NMR analyses the samples were dried at either 200 (calcined 7 and 13 % Si samples) or 360 °C (the steamed 7% Si sample) at low pressure (ca. 1 mm Hg) overnight in a glass equipment enabling inert capping of the NMR rotor. The proton spectra were acquired using two different techniques to reduce background; for the 7 % Si samples the EASY pulse program by Jaeger and Hemmann [25] and for the 13 % Si sample the method reported by Chen et al. were used [26]. Single pulse experiments were the main method used for the ^{27}Al, ^{29}Si, and ^{31}P spectra. For the Al spectra we applied a $\pi/12$ pulse, 10000 scans, and a recycle delay of 0.5 s. The ^{31}P spectra were acquired using a 90° pulse, 100 scans and 30 s recycle delay. For the Si spectra we used 80 scans with a recycle delay of 900 s for the calcined and the steamed sample, while for the as-synthesized samples the recycle delay was 3600 s. The spin-lattice relaxation time parameter T1 of ^{29}Si was not measured, however the absolute intensities of the spectra were evaluated at different recycle delays to ensure data suited for reasonable quantifications. One ^{29}Si single pulse experiment was carried out on the steamed sample with 4000 scans and a recycle delay of 90 s (100 hours exp. Time). ^{1}H-^{29}Si cross polarization (CP) spectra were acquired using 2000 scans, a recycle delay of 5 s, and a Hartmann-Hahn contact time of 2500 µs. The chemical shifts were referenced to TMS, 85% H_3PO_4, and $Al(NO_3)_3$ by the substitution method [27]. MestReNova 9.1 was used for curve fitting using pseudo-Voigt functions and for plotting. All the curvefittings (including integrated peaks) of the NMR spectra are shown in the Supplementary Material.

3. Results

3.1 As-synthesized and calcined samples

The two parent samples in this work have a Si content of 7 atomic % and a 13 atomic % measured by EDS. These will be referred to as the 7 % Si and 13 % Si samples respectively. There is a good correspondance between the Si content of the synthesis gel and that of the final framework as measured by EDS. The SEM images (Figure 1) show regular SAPO-34 crystals in the as-synthesised materials.

Figure 1 about here

Figure 2 about here

The powder XRD patterns of the as-synthesised materials (Figure 2) are similar and consistent with phase pure rhombohedral SAPO-34. However, a small, broad peak at d =15.9 Å may be due to a very low amount of triclinic SAPO-34 in the as-synthesised sample (triclinic SAPO-34 becomes rhombohedral when dehydrated [28,29]). Crystallite sizes for the two samples are estimated as 50 (1) nm (7% Si) and 53 (2) nm (13% Si) by the double Voigt method using peak integral breadth [30]. These sizes appear rather small when compared to the SEM images. It must be remembered that firstly, the XRD result is an average for the whole sample and not just the large, well-formed crystals viewed in the SEM, and secondly that diffraction does not necessarily measure the size seen in microscope images, but the size of the distinct ordered crystalline domains. Karwacki et al. have demonstrated using confocal fluorescence microscopy that SAPO-34 crystals are actually made up of six or more intergrown domains [31]. The crystallite size from diffraction would represent the average of these rather than the crystals seen in SEM. Finally, any presence of intergrowth may contribute to underestimation of the crystallite size from XRD. NMR characterization of the as-synthezised samples are reported in Supplementary Material Figure S1 and S2.

In Figure 3 SEM images of the calcined 7% Si is shown. It appears that there are no significant changes upon calcination.

Figure 3 about here

In contrast, the XRD data show differences between the as-synthesized and calcined dry samples, with the main framework peaks increasing in intensity while those governed by the organic template are disappearing. A Pawley fit to the diffraction profile of the calcined 7 % and 13% Si sample is shown in Figure 4. The rhombohedral structure of SAPO-34 has one crystallographic site for silicon/phosphorus, which is consistent with the single peak observed in solid state ^{31}P NMR (Supplementary Material Figure S3, right).

Figure 4 about here

The unit cell volumes of the calcined materials are very similar: 7% Si = 2430.7(3) Å^3; 13% Si = 2428.8(4) Å^3. The calculated crystallite sizes of calcined materials are 81(1) nm (7% Si) and 50(1) nm (13% Si) [32]. Both calcined samples show high BET surfaces, 708 m^2/g and 539 m^2/g for the 7% Si and the 13% Si samples respectively. Single pulse ^{27}Al and ^{31}P NMR spectra of the calcined samples indicate quite well-defined structures with Al and P atoms in tetrahedral positions and a rhombohedral SAPO-34 material; see Supplementary Material Figure S3 for these spectra. The ^{29}Si NMR spectra show some changes with calcination and drying, consistent with removal of template and adsorbed water. The leftmost peaks for the as-synthesized materials (isolated Si, Si(4Al)) are shifted by ~ 3 ppm in the calcined samples from -91.3 to -94.3 ppm. For the 13% Si sample the calcination and drying resulted in that the five clear peaks in the as-synthesized version become four somewhat broader peaks (see Figure 7a and 7b for the ^{29}Si spectra of the calcined 7% and 13% Si materials respectively). There is a larger right shift of the isolated Si peak than for the other peaks as the rightmost Si peak (-111.1 ppm), assigned to be from Si(0Al), only shifts 0.8 ppm after the calcination and drying, indicating that these Si atoms are less influenced by template and water removal.

3.2 Steamed 7% Si sample

After steaming, the biggest changes were observed in the ^{1}H and ^{29}Si NMR spectra. We did not observe any significant changes in morphology or crystallinity based upon SEM images (Figure 5) nor did we observe any major differences in the X-ray diffraction (Figure 6).

Figure 5 about here

Figure 6 about here

Pawley fit to the XRD data shown in Figure 6 revealed a slight contraction of the unit cell after steaming, with V = 2422.6(3) Å^3 (8.1 Å^3 less than analysed for the freshly calcined sample). The crystallite size is virtually unchanged at 80(1) nm, suggesting little loss of crystallinity after steaming and the steaming has most likely not lead to any increase in microstrain in the crystallites. The BET surface of the steamed sample was 255 m^2/g. Due to small amount of powder and that there was some SiC mixed in after the DRIFTS experiment the reported BET value is on the low side. SiC was measured to have a BET surface of 0.2 m^2/g. A reduction of BET surface has taken place but there is still quite some amount left. Results from all XRD fittings are summarised in Table S1 in the Supplementary Material.

The ^{27}Al NMR spectrum showed very little change (if any at all) after steaming, however there are some minor, still interesting differences in the ^{31}P spectrum. The ^{27}Al spectra are reported in Supplementary Material Figure S10. Figure 7 shows a stacked plot of various ^{29}Si NMR experimental data with the two calcined samples in the three uppermost traces and the steamed sample in the two lowest traces.

Figure 7 around here

In Figure 7 a) and b), spectra of the two calcined samples are shown and it is clear that the 13% sample contains many non-isolated Si atoms, i.e. Si-islands, presented by the big peaks at lower shift values. Figure 7 c) is a ^{1}H-^{29}Si CP experiment that show Si relative close to Hs. As expected there is a decline in H-Si proximities to the right in the spectra. This is in line with the

interpretation that the rightmost peak at -111 ppm is from Si surrounded by 4 Si tetrahedral units. Figure 1 d) shows a [29]Si single pulse spectrum of the steamed sample. By accumulating 4000 scans and using long recycle delay we obtained a good signal-to-noise ratio that enabled a detailed curve fitting (reported in Supplementary Material, Figure S13) with ten well-defined peaks with the following chemical shift values (ppm): -88.4, -92.6, -94.5, -99.5, -101.8, -107.3, -111.4, -115.1, -118.4, and -120.0. In Figure 7 e) a [1]H-[29]Si CP experiment of the steamed sample is shown and it is clear that there are no significant [1]H-[29]Si connectivities at shift values lower than about -100 ppm lending support that peaks at lower shift values originate from Si(4Si,0Al) units, since Q^{1-3} Si-units (Si with e.g. bonded hydroxyl groups) give strong CP signals. Furthermore, by comparing and normalizing the left shoulders in the d) and e) spectra (shown in inset) it can be concluded that the left part is enhanced compared to the Brønsted site Si. In contrast, if normalizing the main peaks in these spectra one can see that they are not fully overlapping indicating a multitude of Si environments in this region. However, further detailed analyses could easily become too speculative and hence are omitted. In addition the -peak centered at -88.4 ppm is broad (a factor of 4-7 times broader than the other peaks) possibly indicating that this region can be assigned to Q^3 species with a broad distribution of local geometries. Table 2 summarizes and compares the chemical shifts with selected ^{29}Si NMR data from literature, where some are selected due to their low chemical shift values (around -120 ppm). One additional relevant compound in this context is tridymite, however, at room temperature monoclinic tridymite has 12 peaks and these do not explain the currently observed spectra [33].

Table 2. Summary of observed [29]Si chemical shift values for current SAPO-34 samples and some relevant [29]Si ppm shift values from literature. (Very)Small peaks are reported in *italics*.

Sample	[29]Si chemical shift values [ppm]									
7% as-synth		-91.3	-95.0	*-99.7*	*-104.9*	*-109.7*				
7% calcined			-94.3	-99.9	*-105*					
7% steamed	-88.4	-92.6	-94.5	-99.5	-101.8	-107.3	-111.4	115.1	-118.4	-120.0
13% as-synth		-91.3	-95.0	-99.6	-104.7	-109.7				
13% calcined			-94.3	-100	-105.6		-111.0			
Chabazite (low Al)[16,34]			-94.0	-99.4 -100	-104.8 -105		-110.0 -111			
Coesite[33]						-108.1		-113.9		
Cristobalite[33]						-108.5				
Quartz[33]						-107.1				

Silicalite[16]						-109.2		-116.3		
Siliceous Ferrierite[35]						-111.8 -112.1		-116.1 -116.3 -116.8		
ZSM-39[36]						Estimated: -107.9		Estimated: -115		Three estimated: around -121

Furthermore the -94.4 ppm peak is assigned to isolated Si responsible for Brønsted acidic sites, (Si(0Si,4Al)), while the next peak at -99.5 ppm is likely due to Si(1Si,3Al). The next peak is a strong one at -101.8 partly overlapping with the peak at -99.5. Interestingly, for this steamed sample the quite common peak observed around -105 ppm in the other spectra or in CHA is absent. The next peak at -107.3 is a new peak and not seen in the other samples. The peak at the chemical shift of -111.4 is assigned to be Si(4Si,0Al) in CHA framework positions, but there is a slightly shift which may originate from local distortions not common in regular CHA framework materials. To assess the three peaks at the most negative chemical shifts in the spectrum of the steamed sample we have employed the equations presented by Ramdas and Klinowski [16]. From these equations one can calculate that the -115.1, -118.4 and -120.0 ppm peaks could be from Si-tetrahedral units with a T-O-T angle of 157°, 165°, and 173° to other Si-tetrahedral units, respectively. Ferrierite or ZSM-39 have local components that could be similar to some of those we observe. In Supplementary Material Figure S15 all the ^{29}Si NMR spectra are shown in stacked mode.

Figure 8 shows a stacked plot of ^{1}H NMR spectra of the two calcined samples (7% Si in a) and 13% Si in b) and the steamed 7% Si sample, c)

Figure 8 around here

The ^{1}H NMR spectra of the calcined samples (a and b spectra) are rather similar. Both samples show a major peak around 3.7-3.8 ppm, typical for bridging hydroxyls in Si-OH-Al groups, i.e. the Brønsted acidic sites [37,38,39,40,41]. The peak in the 7% Si sample is rather symmetric but has a broad underlying feature at 4.9 ppm (based on curve fitting provided in Supporting Material). This latter may indicate Brønsted sites within strongly hydrogen bonded environments,

as discussed by e.g. Huo et al. [42]. In the 13% Si sample the 3.8 ppm peak is asymmetric and curve fitting indicates peaks at 3.7 and 3.9 ppm with an underlying broad band centred at 4.1 ppm. This shows that we are able to observe at least two distinct regular Brønsted acidic sites in the 13% Si sample. Peaks at lower shift values than 3.8 ppm are attributed to OH-groups bonded to the framework [43]. The peaks around 1.7 ppm have previously been assigned to P-OH units [44], but in a work by Bronnimann et al. with fumed silica the peak at 1.7 ppm was reported to be from isolated Si-OH units [45]. Shen et al. reported Al-OH and Si-OH signals at 2.6 and 1.6 ppm, respectively [38].

The ^{1}H NMR spectrum of the steamed sample showed significant changes. The main peak is still intact, as expected since the ^{29}Si NMR data shows a peak corresponding to isolated Si, but there are several small peaks and a big broad feature underlying the whole spectrum. It should be noted that a higher temperature was needed (360 °C) to resolve the ^{1}H spectrum for the steamed sample compared to the unsteamed sample (200 °C). This could indicate the presence of strongly hydrogen bonded OH-unit networks in the steamed sample. This is supported by Bronnimann et al., who argued, based on their data, that their heating at 200 °C and low pressure sample preparation was more than enough to remove physisorbed water [45]. The new and/or more intense peaks at lower shift values are probably newly formed Al-OH, Si-OH, and P-OH groups. Interestingly there is a sharp peak at -0.2 ppm. Unpublished work from our lab on 2D ^{1}H-^{31}P NMR coupling experiments on related samples show that this low shift peak is from protons close to P atoms. In contrast to our interpretation, it is reported by Mastikhin et al. in a review on ^{1}H NMR of heterogeneous catalysts that in γ-alumina a peak at -0.2 ppm was ascribed to OH groups coordinated to octahedral Al [37].

Interpretations of the peaks with the highest chemical shifts are uncertain. Strong interactions of OH groups with local surroundings either with other OH groups or the lattice oxygen atoms, will result in higher shift values and broader peaks relative to a more isolated case exemplified with the fact that a free water molecule has a chemical shift value around 0.3 ppm while H_2O in water have a shift value of 4.78 ppm [46]. Grey et al. reported that water clusters and clusters of water and hydroxonium ions are deshielded due to strong hydrogen bonding with resulting high ppm

shift values in H-ZSM-5 [47]. However, our preparation procedure should have had all physisorbed water removed.

Small but clear changes in the ^{31}P spectrum for the steamed 7% Si sample are evident from Figure 9 when superimposing the spectra for the calcined and steamed samples.

Figure 9 around here

Except for a very minor peak around -10 ppm there are some new shoulders at lower chemical shift values. Since the shoulders are close to the main tetrahedral P peak they might originate from P atoms close to defects in the structure caused by the steaming.

A series of DRIFT experiments of the steamed sample, and its parent calcined version, were carried out while dosing CO in order to investigate the potential effects steaming had on the Brønsted acidic sites, i.e. the acidity. The spectrum for a sample without adsorbed CO was used as background, hence bands from fragments coordinated to CO appear positive (pointing upwards), while the negative bands (pointing downwards) are due to the newly formed fragments.

Figure 10 about here

The DRIFTS data for the steamed sample is in general similar to the parent calcined material. In accordance with earlier reports on HSAPO-34, we observe two major bands that can be assigned to high frequency (HF, 3625-3630 cm^{-1} and being most intense) and low frequency (LF, 3596-3603^{-1}) modes of bridging OH-groups with Brønsted acidic character [48]. This rather general observation compares well to the studies by Smith et al. who were the first to report the HF band at 3630 cm^{-1}, the LF band at 3601 cm^{-1}, and a band at 3610 cm^{-1} [49]. Later, Bordiga et al. reported two HF bands at 3630 cm^{-1} and 3627 cm^{-1}, and a LF-band at 3601 cm^{-1} [50]. Another work by Martins et al. is particlarly relevant to our work because they reported three distinct Brønsted sites based on IR -active bands in the range 3631-3599 cm^{-1} and the values of the peaks agree well with our values reported in Table 3 [51]. However, a new interesting finding comes

out from our curve fitting the Brønsted acidic site region of the spectra. In order to obtain a good fit to the spectra four functions were needed. These four bands are are reported in Table 3. Curvefittings of the spectra are shown in Supplementary Material Figure S4(calcined sample) and S11(steamed sample).

Table 3. Peak position for bands assigned to OH-sites in the calcined 7% Si material and for the same sample after steaming. All wavenumbers are given in cm^{-1}.

Sample id:	HF-band	Intermediate bands		LF-band
	OH_A	OH_B	OH_C	OH_D
7% Si calcined	3625	3618	3609	3596
7% Si steamed	3626	3615	3610	3599

To the best of our knowledge, this is the first experimental observation that indicates the simultanous presence of four sites of possible acidic character in calcined and dried HSAPO-34, using FTIR and CO as a probe molecule. Note, that this does not necessarily imply that there are four different crystallographic positions for acidic protons. A reason for this apparent discrepancy with literature may be that we have used a lower pre-treatment temperature than often reported (e.g. 500 °C in refs. 40). An additional interesting feature is that we observed initial formation of a band at 3634 cm^{-1} (calcined) and at 3630 cm^{-1} (steamed) upon CO exposure, but these band gradually disappeared and actually began pointing upwards as CO was further dosed into the cell. This observation can be interpreted together with the ^{1}H NMR data as follows: The NMR data shows broad features that are likely due to hydrogen bonded OH groups. If CO arrives at such a cluster it adsorbs and breaks up the hydrogen bonded network. This event releases the other protons and this is shown in the plotting of the DRIFTS data as that new Brønsted sites are formed. As more CO is adsorbed these species then disappear, hence explaining that the bands inverts and end up as pointing upwards. The steamed sample even shows a higher intensity of the upwards band which is in correspondance with the bigger broad feature in the sample's ^{1}H NMR spectrum.

4. Discussion

SEM, XRD, DRIFTS, and NMR of ^{29}Si enriched samples have been applied with the objective of identifying structural changes (mechanism and geometry) that have taken place after 1 week steaming of an industrially relevant SAPO-34 (catalyst) sample. Our main observations are:

1) According to SEM images there were no significant changes in particle morphology after steaming.
2) XRD data showed that after steaming the SAPO-34 framework is intact but with a slight unit cell contraction.
3) DRIFTS data do not indicate large differences after steaming.
4) ^{1}H and ^{29}Si NMR data show changes after steaming. Both Si-islands and Si-aggregates have formed, and new broad features appear in the ^{1}H spectrum

The applied calcination and steaming conditions appears to not alter the crystal morphology. However, XRD data show a decrease in unit cell volume after steaming, thus some restructuring at the atomic level must have taken place. Rearrangement of the T-atoms to form Si-islands or Si-aggregates will indeed lead to a change in the average bond lengths and angles. On the other hand, one may question whether an overall reduction in volume is to be expected if the Si-content in the framework remains unchanged, i.e. just redistributed in the framework. Alternatively Si may have left the structure with a resulting reduction in volume, however, this must necessarily also imply significant rearrangement for some Al- and P-atoms.

The Brønsted sites were studied with DRIFTS and ^{1}H NMR and, except for concentration differences (assessed from NMR) the DRIFTS data do not indicate much change in the type of Brønsted acidity. This similarity is in our interpretation due to the fact that those Brønsted sites that actually are remaining after the steaming have not changed significantly. This complies with the ^{1}H and ^{29}Si data, which show that there are still Brønsted protons and isolated Si left after steaming. New features are not of Brønsted acidic character and new Si structures do not have attached protons (evidenced from the ^{1}H-^{29}Si sepctrum of steamed sample). However, an indication of the amount of Brønsted acidic sites that have been lost can be evaluated from ^{29}Si

NMR. From curve fitting ^{29}Si NMR spectra one can estimate that about 85 % of the total Si content is observed at -94.3 ppm for the calcined 7% sample. The rest are in a small peak at -99.9 ppm and in some broad features at even lower shifts. By integrating the ^{29}Si single pulse experiments shown in Figure 1 d) (with known slight underestimation of the Si-island signals) it is evident that the peak at -94.4 now only constitutes about 37% of the total Si content. Due to the known underestimation of Si-island/Si-aggregates this number should be a few percent points lower. This translates into a reduction in Brønsted acidity of more than 50 %.

Big changes have taken place from the Si atom's perspective and after steaming most of the Si atoms reside in new positions compared to the calcined state. As indicated in the introduction, we divide Si clusters into two types: 1) Si-islands (Si-atoms in tetrahedral units that are neighbours in the original SAPO/CHA framework), or 2) Si-aggregates (Si-atoms that are not in the original CHA framework positions). In the last case the channel system/framework type could play a role on dictating morphology by e.g. directing diffusion paths of mobile units. If Si-clusters of type 1 are formed new peaks should be in CHA positions and to identify possible type 2 Si-features one can compare observed data with ^{29}Si NMR of polymorphs of silica. ^{29}Si NMR data suggests that there are new Si(4Si, 0Al) in CHA framework positions due to the peak at -111.4 ppm, while the -107.1 ppm peak could point to a part resembling quartz (at least when considering chemical shift values). The structural features evidenced by the peaks at -115.1, -118.4 and -120.0 ppm are also likely not in the original SAPO-34(CHA) framework. Note further that Si(3Si, 1Al) in CHA should be at -105, which is basically a spot in the Si spectrum of the steamed sample with no intensity.

5. Conclusion

The aim of this work was to gain more insight into structural changes in SAPO-34 from hydrothermal treatments, since this is an important factor for permanent deactivation. A main tool in this work was ^{29}Si solid state NMR, since Si is responsible for the acidic sites in SAPO catalysts. Therefore, we developed a synthesis route utilizing pure ^{29}Si isotopic sources, resulting in 100% ^{29}Si enrichment. The isotopic enrichment of SAPO-34 allowed us, for the first time, to characterise the multiplicity of silicon species in great detail and is a valuable tool in following the subtleties of the migration of the silicon from the framework. The study was performed on three different samples: SAPO-34 with 7 % ^{29}Si, SAPO-34 with 13 % ^{29}Si, and SAPO-34 with 7 % ^{29}Si steamed at 700 °C with a steam partial pressure of 0.7 atm (p total was 1 atm). SEM, XRD and DRIFTS were also used to charcterize the samples.

XRD data showed a reduction of cell volume with steaming, with no associated loss of crystalinity. SEM images did not reveal any changes after steaming. The DRIFTS data showed no big changes after steaming, but results from curvefitting the data indicated that four acidic positions could be present. One or more might be variants of the same site. In addition we observed an interesting phenomen during CO adsorption. This could be interpreted as CO reacting with clusters of hydroxyls/Brønsted sites.

^{29}Si NMR data clearly showed the existence of new and distinct types of local aggregation of silicon after steaming compared to what was observed before. Most of the new Si features did not resemble the Si-islands evident in the as-synthesized/calcined 13% Si, indicating a different form of aggregation, most likely extra-framework. Since the ^{29}Si NMR spectra of as-synthesized Si-islands are very different from the Si-islands/aggregates after steaming there must be different reaction paths during steaming compared to during synthesis for Si-island generation.

To conclude, the nature of Si-island/aggregates formed during hydrothermal conditions has been described and discussed in light of the present data and literature but further work is necessary for understanding the actual processes leading to these Si-islands/Si-aggregates.

6. Acknowledgment

References

[1] B.M. Lok, C.A. Messina, R.L. Patton, R.T.Gajek, T.R. Cannan, E.M. Flanigen, J.Am.Chem.Soc. 106 (1984) 6092-6093.

[2] M. Stöcker, Micropor. Mesopor. Mater. 29 (1999) 3-48.

[3] J.F. Haw, W. Song, D.M. Marcus, J.B. Nicholas, Acc. Chem. Res. 36 (2003) 317-326.

[4] U. Olsbye, S. Svelle, M. Bjørgen, P. Beato, T.V.W. Janssens, F. Joensen, S. Bordiga, K.P. Lillerud, Angew. Chem. Int. Ed. 51 (2012) 5810-5831.

[5] K. Leistner, L. Olsson, Appl. Catal. B 165 (2015) 192-199.

[6] N.O. Chisholm, G.C. Anderson, J.F. McNally, H.H. Funke, R.D. Noble, J.L. Falconer, J. Membr. Sci. 496 (2015) 118-124.

[7] P. Barger, in: M. Guisnet, J.-P. Gilson (Eds.), Zeolites for Cleaner Technologies, Imperial College Press, London, 2002, pp. 239-260.

[8] M. Zokaie, U. Olsbye, K.P: Lillerud, O. Swang, J. Phys. Chem. C. 116 (2012) 7255-7259.

[9] L.R. Aramburo, J. Ruiz-Martinez, L. Sommer, B. Arstad, R. Buitrago-Sierra, A. Sepulveda-Escribano, H.W. Zandbergen, U- Olsbye, F.M.F. de Groot, B.M. Weckhuysen, ChemCatChem 5 (2013) 1386-1394.

[10] T. Fjermestad, S. Svelle, O. Swang, J. Phys. Chem. C 119 (2015) 2073-2085.

[11] T. Fjermestad, S. Svelle, O. Swang, J. Phys. Chem. C 119 (2015) 2086-2095.

[12] Z. Li, J. Martínez-Triguero, J. Yu, A. Corma, J. Catal. 329 (2015) 379-388.

[13] G. Sastre, D.W. Lewis, C.R.A. Catlow, J. Phys. Chem. B 101 (1997) 5249-5226.

[14] E. Lippmaa, M. Mägi, A. Samoson, G. Engelhardt, A.-R. Grimmer J. Am. Chem. Soc. 102 (1980) 4889-4893.

[15] E. Lippmaa, M. Mägi, A. Samoson, M. Tarmak, G. Engelhardt, J. Am. Chem. Soc. 103 (1981) 4992-4996.

[16] S. Ramdas, J. Klinowski, Nature 308 (1984) 521-523.

[17] R. Vomscheid, M. Briend, M. J. Peltre, P. P. Man, D. Barthomeuf, J. Phys. Chem. 98 (1994) 9614-9618.

[18] M.M. Mertens, World Patent 2009/117186, February 6, 2009.

[19] W. Sinkler, R. Broach, N. Erdman, T. Reynolds, J. Chen, S. Wilson, P. Barger, US Patent 2007/0004950, January 4, 2007.

[20] G.S. Pawley, J. Appl. Cryst. 14 (1981) 357-361.

[21] A.A. Coelho, TOPAS V4.1, Bruker AXS, 2006

[22] H. Gies, H. van Koningsveld, Catalog of Disorder in Zeolite Frameworks: http://www.iza-structure.org/databases/

[23] W.A. Sławiński, D.S. Wragg, D. Akporiaye, H. Fjellvåg, Micropor. Mesopor. Mater. 195 (2014) 311-318.

[24] P. Stephens, J. Appl. Cryst., 32 (1999) 281-289.

[25] C. Jaeger, F. Hemmann, Solid State Nuc. Magn. Reson. 57-58 (2014) 22-28.

[26] Q. Chen, S.S. Hou, K. Schmidt Rohr, Solid State Nuc. Magn. Reson. 26 (2004) 11-15.

[27] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow, P. Granger, Solid State Nuc. Magn. Reson. 22 (2002) 458-483.

[28] N. Rajic, R. Gabrovsek, A. Ristic, V. Kaucic, Thermochimica Acta, 306 (1997) 31-36.

[29] A. Tuel, S. Caldarelli, A. Meden, L.B. McCusker, C. Baerlocher, A. Ristic, N. Rajic, G. Mali, V. Kaucic, J. Phys. Chem. B 104 (2000) 5697-5705.

[30] D. Balzar, Voigt-function model in diffraction line broadening analysis, in: R.L. Snyder, H.J. Bunge, J. Fiala (Eds.) Microstructure Analysis from Diffraction, International Union of Crystallography1999.

[31] L. Karwacki, E. Stavitski, M.H.F. Kox, J. Kornatowski, B.M. Weckhuysen, Angew. Chem. Int. Ed. 119 (2007) 7366-7369.

[32] D. Balzar, in: R.L. Snyder, H.J. Bunge, J. Fiala (Eds.), Voigt-function model in diffraction line broadening analysis, Defect and Microstructure Analysis from Diffraction, International Union of Crystallography, Oxford University Press, New York, 1999, pp. 94-126.

[33] J.V. Smith, C.S. Blackwell, Nature 303 (1983) 223-225.

[34] E. A. Eilertsen, B. Arstad, S. Svelle, K. P. Lillerud, Micropor. Mesopor. Mater. 153 (2012) 94-99.

[35] R. E. Morris, S. J. Weigel, N. J. Henson, L. M. Bull, M. T. Janicke, B. F. Chmelka, A. K. Cheetham, J. Am. Chem. Soc. 116 (1994) 11849-11855.

[36] C.A. Fyfe, H. Gies, Y. Feng, J. Am. Chem. Soc. 111 (1989) 7702-7707.

[37] V.M. Mastikhin, I.L. Mudrakovsky, A.V. Nosov, Prog. Nucl. Magn. Reson. Spectrosc. 23 (1991) 259-299.

[38] W. Shen, X. Li, Y. Wei, P. Tian, F. Deng, X. Han, X. Bao, Micropor. Mesopor. Mater. 158 (2012) 19-25.

[39] M. Hunger, D. Freude, D. Fenzke, H. Pfeifer, Chem. Phys. Lett. 191 (1992) 391-395.

[40] A. Buchholz, W. Wang, M. Xu, A. Arnold, M. Hunger, Micropor. Mesopor. Mater. 56 (2002) 267-278.

[41] Y. Jiang, J. Huang, W. Dai, M. Hunger, Solid State Nuc. Magn. Reson. 39 (2011) 116-141.

[42] H. Huo, L. Peng, C. L. Grey, J. Phys. Chem. C 113 (2009) 8211-8219.

[43] D. Freude, H. Ernst, I. Wolf, Solid State Nuc. Magn. Reson. 3 (1994) 271-286.

[44] B. Zibrowius, E. Löffler, M Hunger, 12 Zeolites 1992 167-174.

[45] C. E. Bronnimann, R. C. Zeigler, G. E. Maciel, J. Am. Chem. Soc. 110 (1988) 2023-2026.

[46] B. E. Mann, NMR and the periodic table, (Eds.: R. K. Harris, B. E. Mann), Academic Press, London, 1978

[47] H. Huo, L. Peng, C. P. Grey, J. Phys. Chem C 113 (2009) 8211-8219.

[48] L. Marchese, J. Chen, P. A. Wright, J. M. Thomas, J. Phys. Chem. 97 (1993) 8109-8112.

[49] L. Smith, A. K. Cheetham, L. Marchese, J. M. Thomas, P. A. Wright, J. Chen, E. Gianotti, Catal. Lett. 41 (1996) 13-16.

[50] S. Bordiga, L. Regli, D. Cocina, C. Lamberti, M. Bjørgen, K. P. Lillerud, J. Phys. Chem. B 109 (2005) 2779-2784.

[51] G. V. A. Martins, G. Berlier, C. Bisio, S. Coluccia, H. O. Pastore, L. Marchese, J. Phys. Chem. C 112 (2008) 7193-7200.