



In situ ^{119}Sn -Mössbauer spectroscopic study on MFI, MEL, and MTW tin silicalites

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MFI, MEL, and MTW analogue tin silicalites were studied by *in situ* Mössbauer spectroscopy to complement previous studies. Series of 77 and 300 K spectra were obtained from synthesized, reduced, and oxidized samples. Intensity changes of components as a function of temperature ($d \ln A/dT$ values) were also considered in addition to the usual spectral parameters (isomer shift and quadrupole splitting) to evaluate the spectra. The data obtained for Sn(IV) support neither the octahedral nor the extraframework emplacement; instead, dominance of tetrahedral coordination is supported. Upon reduction in hydrogen a Sn(II) component is formed and can be stabilized. A significant portion of Sn(II) can be reoxidized to the Sn(IV) state by a subsequent medium oxidation. In view of the respective $d \ln A/dT$ values and the stabilization of Sn(II), the structural change of edge-sharing $[\text{SnO}_{4/2}]$ tetrahedra is suggested to form Si–O–Sn(II)–O–Si bridges. The existence of these bridges also can be correlated with the catalytic activity of tin silicalites observed in mild oxidation processes. © Elsevier Science Inc. 1997

Keywords: Tin silicalites; isomorphous substitution; structural defects; ^{119}Sn Mössbauer spectroscopy

INTRODUCTION

The replacement of silicon ions in the center of the elemental building tetrahedra in the framework of various zeolite analogues for other four-valent ions has been attempted and successfully attained in several instances. The substitution of silicon for ions of considerably larger ionic radii, e.g., for titanium or tin ($r_{\text{Si}} = 42$, $r_{\text{Ti}} = 68$, and $r_{\text{Sn}} = 71$ pm, respectively), have been reported. These replacements may result in changes of certain properties compared with those exhibited by the pure silicon-based analogue frameworks. These changes may be attributed mostly to structural modifications originating from the insertion of larger cations. It is worth mentioning that tin might be stabilized in the Sn(II) state as well.

A series of Al-free tin silicalites has been synthesized recently with medium-pore MFI, MEL,^{1,2} ZSM-48³ and large-pore MTW⁴ structures. For syntheses tetraethyl-orthosilicate was used, with various organic templates (tetrapropyl- and tetrabutyl ammonium hydroxide for MFI and MEL, diamino octane and pyrrolidine for

ZSM-48, and hexamethylene bis-benzyl dimethyl ammonium hydroxide for MTW). Unit cell dimensions obtained from XRD studies were interpreted as characteristic for a small portion of regular T-site substitution. From MAS n.m.r. on these tin silicalites octahedral coordination of Sn(IV) ions was concluded (and, in accordance, the alternative tetrahedral substitution was not proposed). In framework FT i.r. spectra a new band appeared at 970 cm^{-1} , which was attributed to the presence of Si–O–Sn bonds.^{4,5} Thus, some uncertainty still exists regarding the localization of Sn in tin silicalites.^{2,4}

Interestingly, a particular catalytic feature was observed in parallel catalytic studies: Oxidations of phenol and toluene as well as cresol, xylene, and bulkier naphthalene molecules were catalyzed with tin silicalites in aqueous media by H_2O_2 . In simultaneous measurements no catalytic effect was exhibited by Sn-free silicalite, tin-impregnated silicalite, or SnO_2 in the same reactions.^{1–4,6} Thus, the essential role of Sn located in the zeolite structure was proved in the oxygen transfer. The role of well-dispersed Sn(IV) present in the channels⁴ as well as the participation of Si–O–Sn groups are suggested in these catalytic processes.⁶

As a characterizing method, Mössbauer spectroscopy might also be a useful tool for collecting more information on the close vicinity of tin ions located in sili-

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Table 1 Mössbauer data extracted from 300 and 77 K spectra of tin silicalites

| Sample | Treatm. | Comp. | 300 K | | | | 77 K | | | | $-d \ln(A_{300}/A_{77})/dT \times 10^{-2}$ |
|--------------------|--------------------|--------------------|---------------------------|--------------|----------|-------------|--------------|--------------|----------|-------------|--|
| | | | IS ^a (mm/s) | QS (mm/s) | S (%) | A (a.u.) | IS (mm/s) | QS (mm/s) | S (%) | A (a.u.) | |
| MFI | synt. | Sn ^(IV) | -0.20 | 0.57 | 100 | 4.587 | -0.16 | 0.66 | 100 | 11.943 | 0.435 |
| Si/Sn= | 400/H ₂ | Sn ^(IV) | -0.15 | 0.59 | 42 | 0.826 | -0.16 | 0.55 | 22 | 2.468 | 0.498 |
| | | Sn ^(II) | 2.84 | 2.03 | 58 | 1.152 | 2.89 | 2.06 | 78 | 8.831 | 0.930 |
| =90 | 250/air | Sn ^(IV) | -0.15 | 0.61 | 71 | 2.469 | -0.08 | 0.63 | 55 | 6.413 | 0.434 |
| | | Sn ^(II) | 2.87 | 2.01 | 29 | 0.985 | 2.95 | 2.12 | 45 | 5.352 | 0.770 |
| MEL | synt. | Sn ^(IV) | -0.22 | 0.44 | 100 | 3.389 | -0.18 | 0.48 | 100 | 6.756 | 0.313 |
| Si/Sn= | 400/H ₂ | Sn ^(IV) | -0.24 | 0.44 | 74 | 1.800 | -0.19 | 0.43 | 51 | 3.529 | 0.306 |
| | | Sn ^(II) | 2.78 | 1.98 | 26 | 0.637 | 2.86 | 1.98 | 49 | 3.421 | 0.765 |
| =50 | 250/air | Sn ^(IV) | -0.21 | 0.46 | 87 | 2.531 | -0.16 | 0.49 | 79 | 5.349 | 0.340 |
| | | Sn ^(II) | 2.89 | 1.98 | 13 | 0.375 | 2.89 | 1.99 | 21 | 1.443 | 0.612 |
| MTW | synt. | Sn ^(IV) | -0.16 | 0.54 | 100 | 1.747 | -0.14 | 0.62 | 100 | 4.999 | 0.478 |
| Si/Sn= | 400/H ₂ | Sn ^(IV) | -0.16 | 0.65 | 74 | 0.765 | -0.15 | 0.73 | 47 | 2.132 | 0.466 |
| | | Sn ^(II) | 2.80 | 1.96 | 26 | 0.274 | 2.92 | 2.09 | 53 | 2.432 | 0.992 |
| =100 | 250/air | Sn ^(IV) | -0.13 | 0.58 | 78 | 0.987 | -0.11 | 0.64 | 64 | 2.961 | 0.50 |
| | | Sn ^(II) | 2.83 | 2.05 | 22 | 0.285 | 2.92 | 2.05 | 36 | 1.646 | 0.797 |
| SnO ₂ + | MFI-Sil | Sn ^(IV) | 0.00 | 0.50 | 100 | 5.877 | 0.04 | 0.55 | 100 | 7.407 | 0.105 |

^a IS, isomer shift, relative to SnO₂; QS, quadrupole splitting; S, relative spectral area; and A, intensity, relative to the base line.

calites. The method has been successfully applied to characterize the alumina-⁷ and silica supported⁸ as well as impregnated L-zeolite catalysts.⁹ *Ex situ* measurements on tin-substituted SnAPO¹⁰ and MFI structures are also reported.⁵

The primary aims of the present study were to attain more specific information on the possible changes in the oxidation and coordination states of tin, and on the changes in the structure in close proximity to tin ions, and to ascertain whether they can be found on the previously mentioned tetrahedral sites, whether the bonds around them may be disrupted during treatments, and whether octahedral coordination occasionally may occur. To this end, *in situ* reduction/oxidation cycles were performed on the various tin silicalites and a less frequently used parameter, $d \ln A/dT$ (intensity change as a function of temperature), was also considered in the evaluation of the spectra.

EXPERIMENTAL

Tin silicalite samples of MFI (Si/Sn = 90), MEL (Si/Sn = 50), and MTW (Si/Sn = 100) structures were synthesized using tetraethyl-orthosilicate and various templates.^{1,2,4} They have been characterized with a great variety of methods (XRD, XPS, ²⁹Si and ¹¹⁹Sn MAS n.m.r., FT i.r., u.v.-vis spectroscopies, and SEM).²⁻⁴ Catalytic studies were performed during the oxidation of various aromatic compounds (phenol, toluene, cresol, and xylene) by H₂O₂.^{1,2,4,6} For comparison, a mechanical mixture of SnO₂ with regular MFI silicalite (without tin) was also measured.

In situ ¹¹⁹Sn Mössbauer spectra of MFI, MEL, and MTW tin silicalites were recorded at 77 and 300 K sequentially in the as-received state, after a 90-min treatment in flowing hydrogen at 670 K and, finally, after a subsequent 90-min treatment in air flow at 520 K. For comparison 77 and 300 K spectra of a mixture of SnO₂

and tin-free MFI-sil zeolite were also recorded. The scheme of the *in situ* cell is reported in Ref. 11. The isomer shift data are relative to SnO₂ at room temperature. The estimated accuracy of positional data is ±0.03 mm/s. For the fits a Lorentzian line shape was assumed, and no positional parameters were fixed *a priori*.

RESULTS

Data extracted from the 300 K and 77 K spectra of MFI (Si/Sn = 90), MEL (Si/Sn = 50), and MTW (Si/Sn = 100) silicalites after various treatments and from spectra of the mechanical mixture of SnO₂ + MFI-sil are collected in Table 1. The parameters presented are: the isomeric shift, IS; quadrupole splitting, QS; relative spectral contributions, S; intensities of components, A; and in the last column, $-d \ln[A_{300}/A_{77}]/dT \times 10^{-2}$ values. The first three data are the most common parameters; the fourth parameter (A), the intensity, is also easily obtained by a consecutive series of *in situ* measurements. The term $d \ln A/dT$ is proportional to the recoilless fraction (f_a) of the absorber (i.e., the sample). In terms of the Debye description of lattice vibrations $d \ln f_a/dT$ is inversely proportional to the mean-square displacement and the effective mass.¹² Thus, in a first approximation, the value of $d \ln A/dT$ is characteristic of the bonding state of the Mössbauer nuclei. Further details can be found, for example in Ref. 13. For illustration, a series of spectra recorded on the Sn-MFI sample at 300 and 77 K is shown in Figure 1.

The values of IS and QS parameters do not depend strongly on the structure, as the comparison of the respective IS and QS values attests. For Sn(IV), IS = -0.20 (±0.04) and QS = 0.55 (±0.1) mm/s values are typical ones at room temperature, and data obtained at 77 K are also close to these values. For Sn(II), IS = 2.86

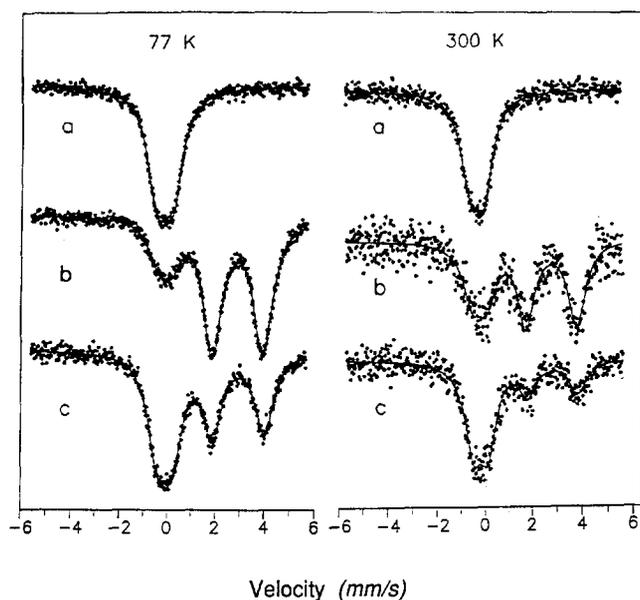


Figure 1 In situ Mössbauer spectra of Sn-Sil (MFI) sample recorded at 300 and 77 K in the as-synthesized state (a), after a 90-min treatment in hydrogen at 670 K (b), and after a subsequent 90-min treatment in air at 520 K (c).

(± 0.03) and $QS = 2.00 (\pm 0.05)$ mm/s values are characteristic at 300 K.

The reduction/oxidation treatments significantly change the Sn(IV)/Sn(II) ratios. The portions of Sn(IV) that can be reduced to Sn(II) by hydrogen in tin silicalites depend on their structure (cf. the S values in Table I). The reduction from Sn(IV) to Sn(II) is more pronounced on MFI, whereas this process is less expressed in MEL and MTW. The portions of Sn(II) components that can be reoxidized to Sn(IV) by air at 520 K are also different; the order of the changing portions is $\text{MFI} > \text{MEL} > \text{MTW}$.

On the other hand, significant amounts of Sn(II) are still retained after the 520-K treatment in air, i.e., considerable portions of Sn(II) are stabilized in each tin silicalite and are not reoxidized to Sn(IV).

The $-d \ln [A_{300}/A_{77}]/dT \times 10^{-2}$ data also provide valuable information. (Their values are slightly different among the samples, most probably due to different effective sample thicknesses, because the Si/Sn ratios are different.) Considering the $d \ln A/dT$ values for Sn(IV), the first important observation is that the values do not change considerably upon the treatments. The other important feature for Sn(IV) is that the $d \ln A/dT$ values obtained for tin silicalites are 3–4 times larger than that obtained for SnO_2 under similar conditions (sample thickness and geometry). The $d \ln A/dT$ values calculated for the Sn(II) component formed upon reduction of tin silicalites in hydrogen are about twice as large as for Sn(IV). It is an interesting feature that these values decrease significantly (by about one-fourth) upon oxidation treatment. In general, for the $d \ln A/dT$ values the $\text{Sn(IV)}:\text{Sn(II)}_{\text{red}}:\text{Sn(II)}_{\text{ox}} \approx 1:2:1.5$ approximate relative ratios can be estimated for each tin silicalite studied.

DISCUSSION

Interpretation of the regular spectrum parameters

To interpret the IS values obtained for the Sn(IV) component the linear combination of the contributions of s - and p -electrons can be considered, as suggested in Ref. 13. The significant negative value (-0.2 mm/s) compared to SnO_2 can be interpreted as the increase of p -symmetry at the expense of the s -symmetry. This feature corresponds to the tetrahedral symmetry of oxide ions around the Sn(IV) ion. Thus, from considering the IS value of Sn(IV), the occupation of framework positions can be suggested. It is worth mentioning that this information is related only to the positioning of the tin ions in the center of building tetrahedra, regardless of the coupling of these tetrahedra.

The IS and QS values obtained for the Sn(II) component after hydrogen treatment are close to each other, probably characterizing similar states of Sn(II) in the various tin silicalites. The obtained values are close to those found in reduced Pt-Sn/alumina catalysts ($2.9 < IS < 3.2$ and $QS = 2.1$ mm/s) that are assigned to Sn-O-Al components.⁷ The values are distinctly different from those characteristic for separate SnO found, for example, on Pt-Sn/SiO₂.⁸ Thus, for Sn(II), the assignment of tin bonded to the zeolite framework via the oxygen bridge can be suggested.

Further, considering the intensity data (A values in Table I) it is worth mentioning that the sums of intensities of tin (IV) and tin (II) components ($\sum A_{\text{Sn}(i)} = A_{\text{Sn(IV)}} + A_{\text{Sn(II)}}$) determined from the 77 K spectra do not vary significantly upon treatment (considering each sample separately). The data indicate that all tin nuclei contribute to the spectra at 77 K, i.e., all sorts of tin are detected and, moreover, there are no other components present in the samples. It might be mentioned here that this condition does not hold for the 300-K spectra (i.e., $\sum A_{\text{Sn}(i)} = A_{\text{Sn(IV)}} + A_{\text{Sn(II)}} \neq \text{const}$; this has the largest value in the as-received sample, the smallest value after hydrogen reduction, and a medium value after the 520-K/air treatment).

Variation of intensity with temperature ($d \ln A/dT$ values)

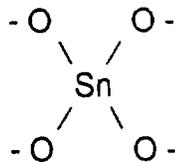
The first consideration of the $d \ln (A_{300}/A_{77})/dT$ values (which are correlated with the recoilless fractions of components) suggests that tin is found definitely in the ionic state in all cases because all the $d \ln A/dT$ values are below 1,¹³ although the values scatter to a certain extent from one sample to the other. (Among other things, the variations may be due partially to different effective sample thicknesses.) The smallest $d \ln A/dT$ value (i.e., the strongest bond) is detected in the sample of $\text{SnO}_2 + \text{MFI-sil}$ mechanical mixture. All the other samples exhibited significantly smaller recoilless fractions (i.e., weaker bonds). Thus, the ionic character and the smaller recoilless fractions for tin(IV) in tin silicalites compared to SnO_2 point also to the tetrahedral coordination of Sn(IV). It should also be noted

that the $d \ln A/dT$ values for Sn(IV) are similar; they do not depend strongly on the treatments applied.

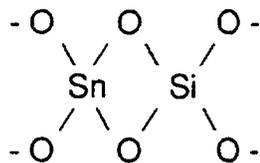
Considering the $d \ln A/dT$ values determined for Sn(II) components, considerably large values are obtained. The values are significantly larger than characteristic for regular SnO.¹³ These values are also large compared with data within tin silicalites: After hydrogen treatment values about twice as large are found for Sn(II) than for Sn(IV). The treatment in air decreased the $d \ln A/dT$ for Sn(II), but even so it remained one and a half times as large as for Sn(IV). The change of the $d \ln A/dT$ for tin(II) is probably related to the finding that a certain amount of tin did not contribute to the spectra at 300 K ($\sum A_{\text{Sn}(i)} \neq \text{const}$ was found). From the combinations of the observations that (1) there were only two species present in the spectra, [Sn(IV) and Sn(II) each with similar parameters in all samples], and (2) the $d \ln A/dT$ values varied solely for tin(II), it may be suggested that more than one Sn(II) component was present in the samples (still with similar IS and QS parameters, i.e., probably in Si–O–Sn links).

Structures assumed

The structural effects of replacement of silicon for ions of larger radii, (e.g., for titanium) were studied by XANES and EXAFS. Besides the regular corner-linked arrangement of tetrahedra other possibilities are also suggested (e.g., edge sharing of adjacent tetrahedra, or formation of 6-membered rings when two tetrahedra are both linked to a third one, etc.).¹⁴ For the insertion of tin, similar structures may be postulated because its ionic size is almost the same as that of titanium. Simple structures have already been considered for interpreting the coordination effects in catalytic processes with MFI tin silicalites⁶ (the regular corner-sharing arrangement, shown in *Scheme 1* and the edge-linked structure in *Scheme 2*). Presumption of these structures coincides with the Mössbauer results: Both structures contain tetrahedral coordination for tin and, in accordance, tetrahedral coordination was found from the IS data for the Sn(IV) component.



Scheme 1



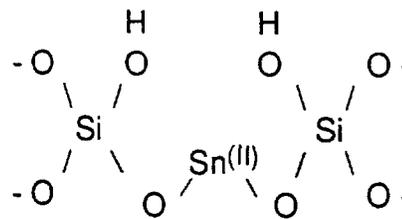
Scheme 2

The treatment of tin silicalites in hydrogen resulted in the decrease of Sn(IV) contributions. Probably the opening of the common edge in the edge-sharing pairs of tetrahedra (*Scheme 2*) is preferred because the Sn–O–Si bond angles are strained in this structure.^{14,15} Thus, the Sn(II) component is probably located in Si–O–Sn–O–Si bridges. This suggestion is in accordance with the observed IS and QS data as proposed for the Si–O–Sn assignment, and it also corresponds to the $d \ln A/dT$ values, which indicate a weakened but still significant ionic bond strength ($d \ln A/dT$ values are below 1). Thus, after hydrogen treatment the presence of the structure shown in *Scheme 3* can be assumed. Reduction of Sn(IV) to Sn(II) should result in an increase of the ionic radius (from 71 to 93 pm) due to the appearance of a lone electron pair. These electrons possess both p and s characters, as the increase of IS and QS values attest. [The hypothetical pure $5s^2$ state would give an IS value of 7.6 mm/s^{-1} , the electric field gradient originates from the significant p_z character of the nonbonding orbital of Sn(II)¹⁶]. Thus, the reduction is accompanied by characteristic structural changes.

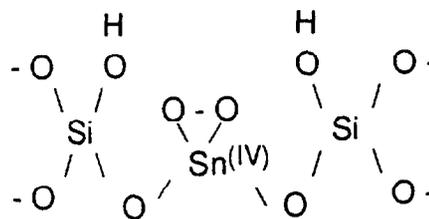
Upon oxidation in air a significant portion of Sn(II) was reoxidized to Sn(IV). Reconstruction of the original strained edge-shared pairs of tetrahedra is probably less pronounced because of the above-mentioned structural changes brought about by the previous reduction. Instead, simple bonding of oxygen to tin(II) can probably be assumed (either as dioxygen, or in monoatomic form). This possibility is also analogous to that suggested for the titanosilicates^{14,15} (*Scheme 4*). The assumed bonding of oxygen may increase the vibrating mass [thereby decreasing the corresponding $d \ln A/dT$ values for Sn(IV), as shown in *Table 1*].

During the treatment in air other structures containing the Sn(II) component may possibly develop because a certain portion of Sn(II) is preserved [and a simultaneous decrease is observed in the $d \ln A/dT$ values for Sn(II)].

Finally, it is mentioned that the catalytic ability of tin



Scheme 3



Scheme 4

silicalites is also in accordance with the considerations presented above: The Sn(II) centers located in the Si–O–Sn–O–Si bridges may provide a site for the reversible fixation of oxygen. At these sites both Sn(IV) and Sn(II) states might be stable by the alteration of +2 and +4 valencies, depending upon the conditions.

CONCLUSIONS

The presence of tin in different oxidation, coordination, and bonding states was revealed by analyzing Mössbauer data obtained from *in situ* spectra recorded after reducing and oxidizing treatments of MFI, MEL, and MTW analogue tin silicalites.

-Sn(IV) was found in a bonded state, with a dominance of tetrahedral symmetry. Thus, primarily framework substitution of Sn(IV) is suggested in the centers of building tetrahedra. The data obtained do not support the assumption of the presence of extraframework Sn(IV) in octahedral coordination.

-A certain portion of Sn(IV) is probably located in distorted structures (e.g., in edge-shared tetrahedra) because Sn(IV) can be partially reduced.

-The IS, QS, and $d \ln A/dT$ data obtained for the Sn(II) component formed agree with the assumption of the existence of Si–O–Sn–O–Si bridges. Upon medium oxidation Sn(II) can be partially reoxidized to Sn(IV), another portion remains stabilized as Sn(II).

-The existence of Si–O–Sn–O–Si bridges could provide an interpretation of the ability of tin silicalites to transfer oxygen in oxidation processes; tin ions are accessible in the bridges and both Sn(IV) and Sn(II) can be stabilized in them, thereby providing a center for redox cycles.

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