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Published version:

DOI:10.1002/cphc.201200893

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ChemPhysChem, ***14*** *(2013) 79-83*

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Preference towards Five-Coordination in Ti Silicalite-1 upon Molecular Adsorption

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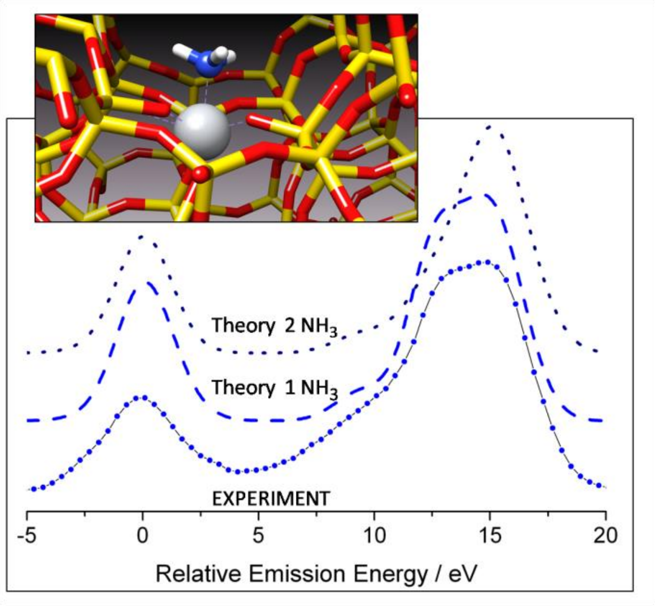
One is enough! The changes of the electronic structure induced by the adsorption of water and ammonia in the catalyst titanium silicalite-1 (TS-1) are investigated by means of (resonant) valence-to-core X-ray emission spectroscopy. Based on spectra simulations using density functional theory it is concluded, contrary to the widely accepted view, that the Ti-sites of TS-1 can coordinate only one molecule of ammonia and water (see picture).



Meso-porous and micro-porous Ti-zeotype materials[1–4] are often good catalysts for selective oxidation reactions and thus of prime importance in petro-chemical industry. Among them, one of the most extensively used is titanium silicalite-1 (TS-1).[5–9] Theoretical and experimental studies on the Ti-sites were carried out using different spectroscopic tools to understand their catalytic behaviour.[6, 7, 10–17]

The average coordination number of Ti in dehydrated TS-1 was found to be close to four and the average Ti–O bond length was established to (1.80±0.05) Å by analyzing the extended X-ray absorption fine structure (EXAFS).[18, 19] EXAFS was also used to address the question raised by IR and Raman spectroscopy concerning the presence of Ti-sites with tripodal and/or tetrapodal arrangements.[4, 7, 11, 12] It was established that Ti is preferentially located inside a tetrapodal structure. EXAFS was then applied to investigate the catalyst under in situ conditions and to understand the mechanism of the catalytic paths[10,12,16,17] using water and ammonia as probe molecules due to their relevance in various catalytic transformations. The EXAFS data were, however, not conclusive[11,19,20] and other techniques, such as micro-calorimetric measurements[21–22] were employed. It was proposed that the Ti coordination number is close to six upon adsorption of water and ammonia.[7,10,21,22] Water and ammonia can also be adsorbed by the zeolite-framework. The Ti-coordination number was obtained by subtracting the calorimetric contribution of a Ti-free silicalite-1 from the TS-1-calorimetric signal but the reliability of the method has been debated.[10, 22]

The problem was then addressed by analyzing the X-ray absorption near edge structure (XANES). Different authors reported the XANES spectra of TS-1 in comparison with the XANES spectra of model compounds.[4,11,12,23] However, XANES measurements do not allow for the disentanglement of geometric and electronic information as both strongly influence the XANES features.[18] Furthermore, the identification of the coordination number using methods presented elsewhere[11,23–26] were found to be non-conclusive for TS-1.

Some of the authors herein recently revisited the problem and performed a non-resonant valence-to-core X-ray emission spectroscopic[27–30] (vtc-XES, see the Supporting Information) investigation of an activated sample of TS-1 (TS-1/act).[31] The vtc-XES data were modelled[32–34] using density functional theory[35] (DFT) calculations assuming a Ti-centred tetrapodal structure[12] including O atoms up to the third coordination shell of Ti. The good agreement between experiment and theory justifies a quantitative analysis of the $K\beta_{2,5}$ region[29] of the vtc-XES spectra and we report in the present study the modification induced on the electronic structure of TS-1 when the catalyst interacts with water (TS-1/H_2O) and ammonia (TS-1/NH^3) (see the Experimental Section).[6,10,36]

Figure 1 shows the vtc-XES of TS-1/act, TS-1/H_2O, and TS-1/NH_3. The Kβ” maximum A blue shifts upon adsorption of water (0.2 eV) and ammonia (0.4 eV) and its intensity decreases (15% and 30%). In addition, the Kβ” region of TS-1/NH_3 shows a low intensity feature, A1 (inset Figure 1), at around 4950 eV. Three main features D, B and C (Figure 1) contribute to the $K\beta_{2,5}$ shape. Upon gas adsorption, D becomes more intense keeping the same shape and intensity for TS-1/H_2O and TS-1/NH_3. B becomes less pronounced and shifts to higher energies, while C varies depending on the kind of ligand: when water (ammonia) is adsorbed it becomes less (more) pronounced.

Insights into the experimental vtc-XES data can be gained from symmetry arguments because the intensities of the vtc- XES spectral features are related to the matrix elements[32,33]

$$<\psi_{\mathrm{Ti(1s)}} \mid \mathbf{e_j}\, \mathbf{r} \mid \psi_{\mathrm{V-MO}}>,$$

where $\mathbf{e_j}$ is a set of three orthogonal unit vectors and $\psi_{\mathrm{Ti(1s)}}$ / $\psi_{\mathrm{V-MO}}$ are the valence- and Ti(1s)-based molecular orbitals (MOs), respectively. The symmetry of the Ti(1s) orbital is totally symmetric and hence the intensity of a vtc transition can be examined using the symmetry of the V-

MOs. Two simple models with octahedral $Ti(OH)_6$ and tetrahedral $Ti(OH)_4$ symmetry (Figure 2) were employed to exemplify this point. The vtc-XES of $Ti(OH)_6$ consists of two main peaks that involve MOs with t_{1u} symmetry, $4t_{1u}$ and $5t_{1u}$ (Figures 2b and SI1). The $4t_{1u}$ and the $5t_{1u}$ MOs have strong O(2s) and O(2p) atomic character. MOs that have ungerade symmetry, that is, give rise to Laporte-allowed transitions, but with small (e.g. $6t_{1u}$) or zero (e.g. $1t_{2u}$) Ti p character (i.e. orbital moment l=1 with respect to the Ti centre) do not significantly contribute to the spectra (Figure 2 and Figure SI1).

The vtc-XES of $[Ti(OH)_4]$ is composed of three peaks. Each peak is associated with MOs with t_2 symmetry and thus Ti p character. We observe that the absence of inversion symmetry and thus the possibility for p–d mixing in T_d symmetry increases the number of observed transitions in the $K\beta_{2,5}$ region of the vtc-XES. Orbitals with Ti 3d character can contribute to the vtc-XES in T_d symmetry, whereas they are absent in Oh symmetry.

It is interesting to note that the observations are different at the K absorption pre-edge where the spectral features become sharper (and more intense) in T_d symmetry as compared to O_h symmetry.[39] The reason is that the absorption pre-edge in perfect O_h symmetry draws its spectral intensity from weak electric quadrupole transitions and the removal of the inversion symmetry allows for strong dipole contributions only for a t_2 symmetry.

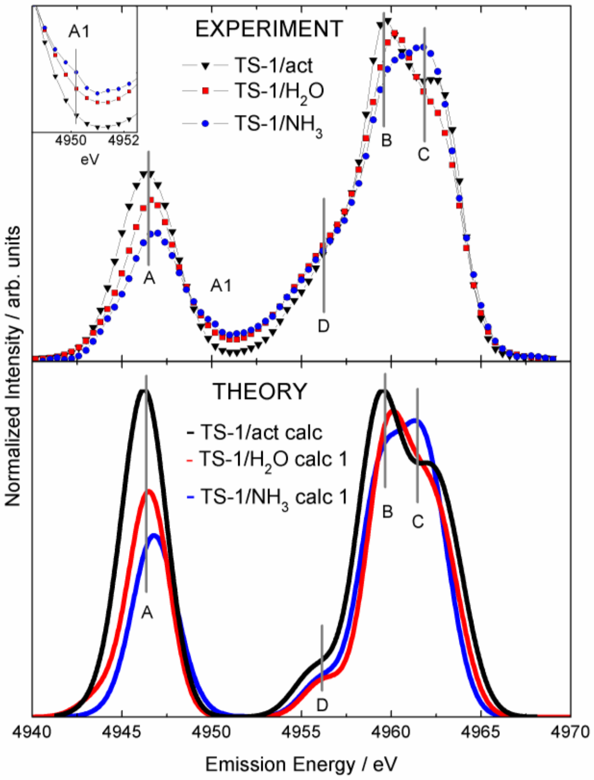


Figure 1. *Top (bottom), experimental (calculated)* valence-to-core X-ray emission spectra of TS-1/act, TS-1/H_2O and TS-1/NH_3. The calculations refer to the models with one adsorbed molecule (calc 1). The energy scale of the calculations has been shifted to match the experimental data.

We compare in Figure 2d the experimental spectra of TS-1/act and of $CaTiO_3$ as examples for Ti^{IV} in local T_d symmetry and for Ti^{IV} in local O_h symmetry to verify the theoretical reasoning. The vtc-XES of $CaTiO_3$ presents a sharp $K\beta_{2,5}$ line in contrast to the double feature in TS-1/act. This is in good qualitative agreement with Figure 2a. We note that the sensitivity of vtc-XES extends beyond the first coordination sphere and the simple theoretical model excludes many effects.[31]

Considering a larger cluster and small deviations from strict O_h local symmetry will reduce some degeneracy and result in broader spectral features.

Figure 3(top) shows a comparison of the experimental and calculated vtc-XES of TS-1/act. In contrast to Figure 2a the cluster that is used for the calculations now contains atoms including the third coordination sphere of Ti.[31] The MOs involved in the vtc-XES transitions have strong ligand character, while the spectral intensity arises from the Ti(p) contribution.

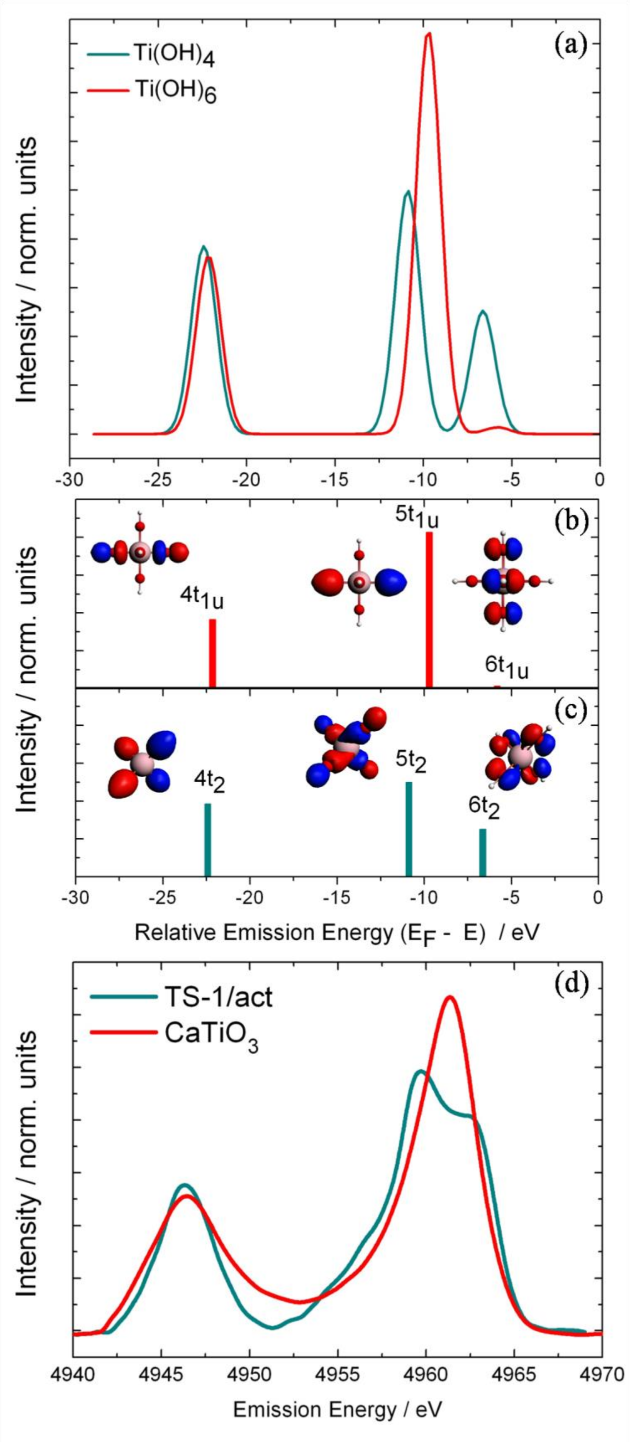


Figure 2. (a) Calculated vtc-XES spectra of $Ti(OH)_4$ (green line) and $Ti(OH)_6$ (red line). (b,c) Intensities for the vtc transitions and significant MOs. (d) vtc-XES of TS-1/act (green line) and $CaTiO_3$ (red line).

An analysis of the MOs (see the Supporting Information) reveals that the main contributions to the Kβ" feature are due to the almost degenerate MOs with strong O(2s) atomic character, while the MOs with O(2p) atomic character mostly contribute to the $K\beta_{2,5}$.

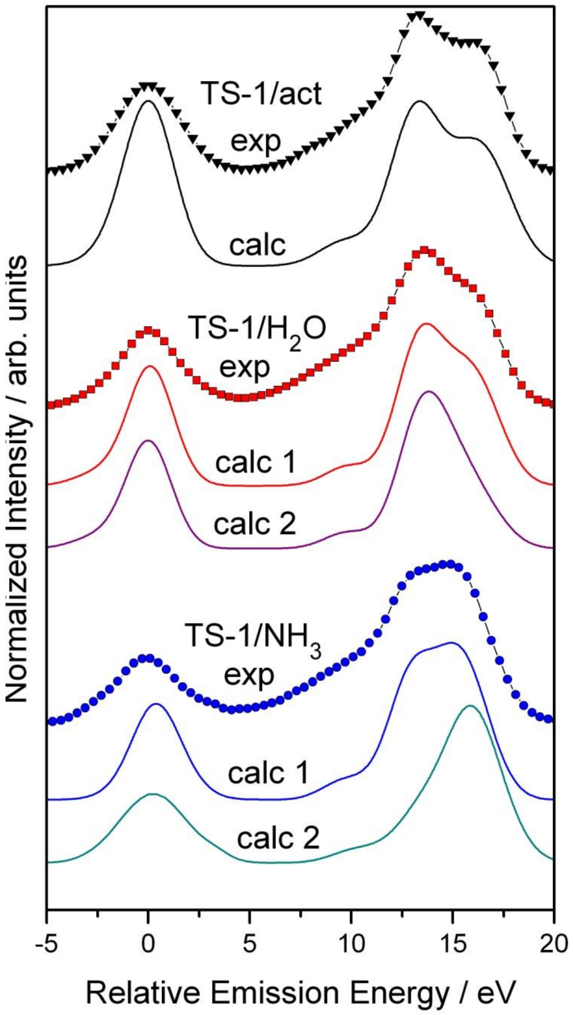


Figure 3. Experimental (exp) and calculated (calc) vtc-XES spectra of TS-1/act, TS-1/H_2O and TS-1/NH_3. We calculated two spectra with one (calc 1) and two (calc 2) adsorbed molecules for TS-1/H_2O and TS-1/NH_3. The vtc-XES spectra are offset along the intensity axis for clarity.

We observe that the $K\beta_{2,5}$ region of TS-1/H_2O(NH_3) has a double feature in contrast to $Ti(OH)_6$ or $CaTiO_3$ (Figures 1 and 2). Figure 3 shows the comparison between the experimental and the computed vtc-XES spectra of TS-1/H_2O (middle) and TS-1/NH_3 (bottom) assuming one (calc 1) and two (calc 2) adsorbed molecules and using clusters that have been proposed elsewhere.[10,13,38,39] The $K\beta_{2,5}$ region exhibits a double feature in the case of one adsorbed molecule in agreement with the experiment. It becomes sharper when the Ti centre is assumed to be six-coordinated, that is, two molecules are adsorbed. This is in agreement with the simplified model that we discussed in the context of Figure 2. The calculated spectra with one adsorbed molecule are compared to each other in Figure 1. We observe that the theoretical vtc-XES of TS-1/act, TS-1/H_2O (calc 1) and TS-1/NH_3 (calc 1) present similar relative changes in intensity as the experimental vtc-XES spectra. When one molecule is adsorbed on the Ti centre the degeneracy of the MOs linked to the main features of the vtc-XES (A, D, B, and C, Figure 1) is removed and new transitions involving MOs with O^{water}(2p) and $N^{ammonia}$(2p) atomic character arise in the $K\beta_{2,5}$ region. The calculation reproduces the shift of the Kβ”region (Figure 1), which we attribute to the presence of transitions involving MOs with $O^{water}(2s)$ and $N^{ammonia}(2s)$ atomic character.

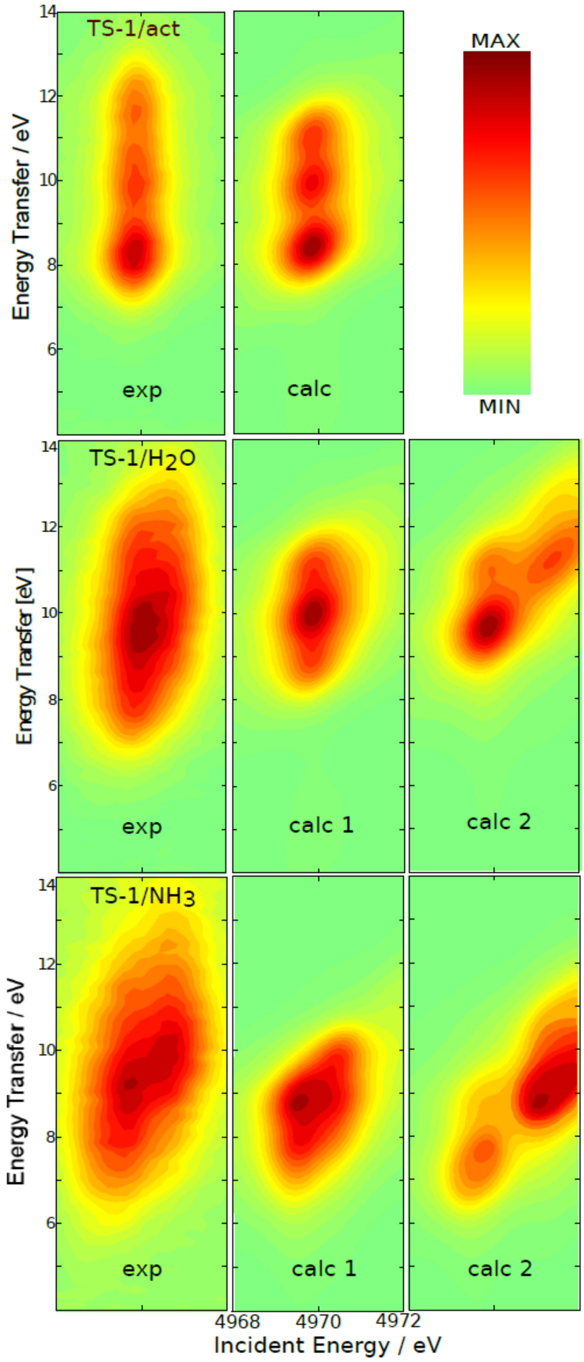


Figure 4. Comparison of the experimental (exp) and calculated (*cf.* Figure 3) rvtc-XES maps of TS-1/act (top), TS-1/H_2O (middle) and TS-1/NH_3 bottom. The colour code is defined by the color bar.

The non-resonant XES data probe occupied orbitals. Previous work that proposed six-coordinated Ti in TS-1 when H_2O and NH_3 are adsorbed used X-ray absorption spectroscopy that relates to the unoccupied electronic levels.[10,11] It is possible to combine X-ray absorption with X-ray emission spectroscopy by resonantly exciting a Ti 1s electron into low-lying unoccupied molecular orbitals.[40] In this way it is possible to study occupied and unoccupied orbitals in one experiment and thus considerably increase the sensitivity to the local coordination. The energy that is transferred to the sample is measured, similar to optical resonance Raman spectroscopy. Resonant vtc-XES (rvtc- XES, see the Supporting Information) allows to record electronic excitations covering and extending the range of UV/Vis measurements, however, with lower spectral resolution. The technique is element-selective and is thus particularly sensitive to ligand-to-metal charge-transfer excitations. We measured and calculated the rvtc-XES maps of TS-1/act TS-1/H_2O and TS-1/NH_3 (Figure 4). We found good agreement between the calculation and the experiment in the case of TS-1/act. The features are mainly due to transitions between molecular orbitals with Ti(p) character having strong O or/and SiO_3 character to molecular orbitals with strong Ti(3d–4p) character. We observe additional spectral intensity at higher incident energy upon adsorption of H_2O or NH_3. This intensity is significantly overestimated when two adsorbed molecules are assumed in the calculations. The agreement between experiment and theory is notably better when only one adsorbed molecule on the Ti centre is considered in the calculations.

Summarizing, we find strong experimental evidence that only one molecule is adsorbed on the Ti centres in TS-1. The evidence is based on element-selective spectroscopic studies that probe the occupied (XES) and unoccupied (XAS) molecular orbitals.

Our conclusion mainly relies on the comparison between experiment and quantum chemical calculations. The recent progress in modelling of XES data using DFT makes this a viable approach that allows for an understanding of the underlying modifications of the electronic structure in great detail.[41] Knowledge of the number of molecules coordinated to the Ti centres in TS-1 under in situ conditions is of paramount importance for understanding the catalytic path of the catalyst and provides crucial inputs for theoretical estimates of efficiency and kinetics of a reaction. It is worth mentioning that in defective Ti-based zeotype materials, such as the recently synthesized Ti-STT,[42] having a lower catalytic attitude than TS-1, the average coordination number of the Ti centres is proposed to be close to six when water is adsorbed. This could be linked to the presence of titanol groups in the framework of such materials.

Experimental Section

The experiments were performed at the beamline ID26 of the European Synchrotron Radiation Facility (ESRF, France). The incident energy was selected by means of a pair of cryogenically cooled Si(311) single crystals. Higher harmonics were suppressed by three Si mirrors operating in total reflection. The beam size on the sample was approximately 1.0 mm horizontally and 0.2 mm vertically. The spectrometer exploits the (331) Bragg reflection of five spherically bent Ge crystals (radius 1000 mm) arranged in a vertical Rowland circle geometry. The emitted photons, selected by the spectrometer, were detected using an avalanche photo-diode. The total energy bandwidth was 0.9 eV. The sample was placed inside an in situ cell oriented at 45° with respect to the incident beam and the X-ray spectrometer crystals. The vtc-XES spectra were measured by tuning the incident energy above the Ti K-edge at 5015 eV and scanning the emitted energy. All data are normalized to the spectral area that includes the $K\beta$ main and the vtc lines. We subtracted the background from the $K\beta_{1,3}$ peak tail by fitting four Voigt-line profiles. Details about this procedure can be found elsewhere.[31,43] The rvtc-XES data were collected by scanning the incident energy across the Ti XANES pre-edge region, while recording the emitted photon energy up to an energy transfer of 15 eV. The spectral features of the rvtc-XES map were then normalized to the maximum of the main peak of the charge-transfer region. The TS-1 sample was supplied by ENI, Instituto G. Donegani (Novara, Italy). The Ti loading was 2.98 wt%, as determined by the cell volume expansion, and the absence of extra phases of TiO_2 was carefully checked. TS-1 was measured in the form of a self-supported pellet inside an X-ray fluorescence cell after degassing at 400 °C (TS-1/act). The same degassing procedure was used for the preparation of TS-1/H_2O and TS-1/NH_3. Vapour pressure of water was adsorbed for TS-1/H_2O. 500 torr pressure of ammonia was adsorbed for TS-1/NH_3. DFT calculations were performed using ORCA 2008, ab initio/DFT code,[44] further computational details can be found elsewhere.[31,45–48]

Acknowledgment
This work has been performed on the ID26 beamline at the European Synchtron Radiation Facility (ESRF), Grenoble, France. We are grateful to Mauro Rovezzi and Christophe Lapras (ESRF, ID26) for their assistance during the experiment and to Rainer Wilcke and Claudio Ferrero (ESRF, Data Analysis Unit) for the support during the calculation.

Keywords: adsorption;·coordination modes; density functional theory; Ti silicalite-1; X-ray emission spectroscopy

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