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Novel titanium sites in silicalites

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Tetra- and pentacoordinated sites are characterized in two titanium silicalites of MEL structure using XANES and EXAFS investigations at the Ti K-edge. A short Ti–Si distance of 2.19 ± 0.05 Å in both samples is consistent with titanium [TiO_x] units sharing edges with [SiO_4] tetrahedral units. This result shows that titanium is located on a framework defect and not in a regular T site.

Keywords: Silicalite; zeolite; titanium; tetrahedral; site; structure; EXAFS; XANES

1. Introduction

Titanium silicalites of ZSM-5 structure [1], designated as TS-1, have received much attention owing to their unique catalytic activity for selective oxidation of hydrocarbons [2–5] attributed to the presence of Ti–O–Si bridges [6,7] and/or titanyl groups [2]. Based on the unit cell expansion [6], it is widely believed that Ti^{4+} ions, like other inserted d-elements, are located in tetrahedral sites in isomorphous substitution [8]. However, recent X-ray absorption fine structure (XAFS) investigations on TS-1 samples show that titanium occupies octahedral and possibly square pyramidal sites as well. The ratio between these sites depends on the sample preparation and the dehydration level [9,10]. This might imply non-substitutional sites for titanium.

Titanium silicalites are characterized by an IR band at 960 cm^{-1} which is assigned to a titanyl group [2] or to a symmetric stretching vibration mode of a [SiO_4] unit attached to a titanium(IV) ion [7]. Behrens et al. showed from the titanium X-ray pre-edge analysis that the titanium ions occupy mostly octahedral sites and only a weak dependence on the dehydration was observed for their TS-1 sample [10]. Conversely, Lopez et al., using successfully the first shell extended X-ray absorption fine structure (EXAFS) analysis, found a strong

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dehydration dependence leading to a transformation from octahedral to tetrahedral sites [9]. The analysis of the second shell of distances not yet attempted for TS materials was, however, already performed for nickel surface silicates [11,12], silica supported copper [13] and titanium glasses [14]. In all these cases, the $[MO_x]$ moieties were found to share corners with $[SiO_4]$ units leading to a M–Si distance of 3.1–3.4 Å. The present work reports on two TS-2 materials most active in the oxyfunctionalization of *n*-hexane [15] and addresses the question as to how the framework titanium is linked to the $[SiO_4]$ units and how the site is located within the framework.

2. Experimental

Two silicalites referred to as 1.6- and 4.2-TS-2 for a Ti/Ti + Si ratio equal to 1.6 and 4.2%, respectively, were synthesized [16], calcined at 773 K and air exposed before characterization. XRD revealed a characteristic MEL structure [17] and a crystallinity higher than 90%. IR spectra of these materials show the characteristic linear dependence between the Ti content and the band at 960 cm^{-1} [15,16]. Two titanium oxides (anatase and rutile) were used as reference compounds for EXAFS analysis [18].

The Ti K-edge measurements were performed in transmission mode using air filled ion chambers at the radiation synchrotron facility of the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE). The white radiation was emitted in a single bending magnet mode by the DCI storage ring and monochromatized by a Si(111) two-crystal monochromator. Sample preparations for XAFS measurements as well as analysis and presentation of the results were performed according to the recommendations of the International Workshops on Standards and Criteria in XAFS [18]. EXAFS spectra analyses were performed using programs [19] designed for standard background treatment and normalization of the pre-edge and post-edge regions [14,18,20,21] EXAFS simulations were performed using McKale theoretical phase and amplitude backscattering functions [22]. The electron inelastic mean free path, λ (Å), was approximated by the empirical equation [21]

$$\lambda = \frac{1}{\Gamma}\left[(\xi/k)^4 + k\right],$$

where ξ (kept constant at 3.1) and Γ are empirical parameters, generally close to one. The accuracy was calculated from the covariant matrix and the experimental signal to noise ratio. Titanium and oxygen shells were fitted with a Γ of 1.0 for reference compounds. Γ was found close to 0.6 for silicon in two nickel silicate references (talc and nepouite) [11,12]; a significant multiscattering contribution is indeed expected to reduce Γ since the Ni–O–Si angle is close to 130°. In the present situation the acute Ti–O–Si angle precludes such contribu-

Table 1
Pre-edge characteristics for air exposed titanium silicalites and various reference compounds

Compound	Symmetry [a]	Position [b] ±0.2 (eV)	Height [b] ±5%	Linewidth [b] ±0.2 (eV)	Area ±10%	Ref.
Ba_2TiO_4	T	2.5	0.84	1.5	1.3	[20]
Ti phthalocyanine	SP	3.5	0.79	1.9	1.5	[20]
kaersutite	distorted O	3.5	0.30	2.7	0.8	[9]
anatase	O	2.3/4.7/7.8	0.13/0.22/0.21	2.2	–	this work, [28]
rutile	O	2.0/4.7/7.8	0.04/0.18/−0.16	2.2	–	this work, [9]
1.9-TS-1	distorted O	3.5	0.27	2.3	0.6	[9]
1.9-TS-1 dehydr.	distorted T	2.8	0.50	1.5	0.8	[9]
x-TS-1 [c]	O+SP+T	3.6 [d]	0.28 [d]	2.9 [d]	–	[10]
1.6-TS-2	T+SP	2.9	0.49	2.0	1.0	this work
4.2-TS-2	T+SP	3.0	0.40	2.3	0.9	this work

[a] T = tetrahedral, SP = square pyramidal and O = octahedral.

[b] The zero of the energy scale was taken at 4964.2 eV which corresponds to the maximum of the first peak of a titanium foil K edge. The zero energy was recalculated for the literature data when the reference point was different. The monochromator was a Si(111) for this work and for ref. [10], while it was Si(220) for ref. [14] and Si(311) for refs. [9,28] respectively. In optimized conditions, the resolution is expected to increase along the Si(111), Si(220) and Si(311) sequence of monochromators leading to narrower and higher peaks; only the area is unchanged. The area are then calculated from heights and linewidths for single peaks.

[c] The Ti/Ti + Si ratio, x, is not provided in ref. [10].

[d] Estimated from a figure of ref. [10]; the broad linewidth includes the unresolved satellite components.

tion and a Γ of 1.0 was taken to simulate the silicon shell. The baseline residue was also fitted to obtain a better quality of fit and first shell simulated distances less dependent on the baseline extraction process (tested on K-edges of various first row d-elements [23]).

3. Results

A decreasing titanium pre-edge intensity is produced by moving from tetrahedral, square pyramidal to octahedral symmetries or, considering the kaersutite, anatase and rutile series, by a decreased distortion of the octahedron (table 1). For comparison, at least qualitatively, of the data of table 1, one has to take into account the difference in the resolution of the various reported measurements and focus on the area of the pre-edge when considering a single peak. The TS-2 silicalite pre-edges exhibit intermediate intensities and positions (fig. 1) in comparison with tetrahedral and octahedral titanium in model compounds. This suggests that our data are the result of a mixture of sites in agreement with previous findings for a TS-1 sample [10]. More intense pre-edges were observed

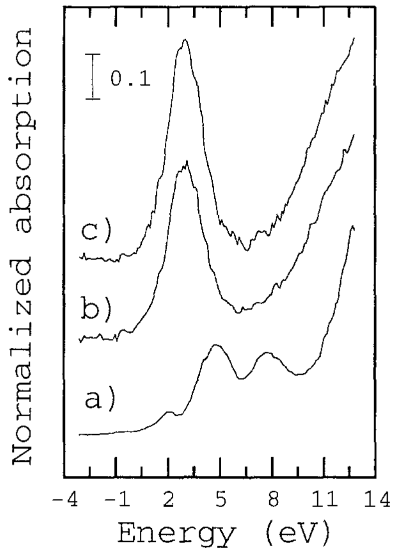


Fig. 1. Normalized Ti K-pre-edges of (a) rutile, (b) 4.2-TS-2 and (c) 1.6-TS-2 samples.

for our hydrated TS-2 samples than for TS-1 samples cited in the literature [9,10] indicating a higher concentration of low coordination sites.

The experimental EXAFS data were first simulated with a single oxygen shell containing 4.8 and 4.0 (± 0.6) atoms at 1.90 and 1.92 (± 0.03) Å for 1.6-TS-2 and 4.2-TS-2 samples (fig. 2). The fit quality was found satisfactory only in a limited range of 2.52–10.1 $Å^{-1}$ in agreement with previous data [9]. The Debye–Waller factor was simulated at too high a value of 0.12 ± 0.05 Å in comparison, for instance, with 0.07 ± 0.02 Å found in anatase. Attempts to fit one or more silicon neighbours at about 3.3 Å (corner sharing type of binding) failed. The comparison of the various simulated environments (see FT signal in fig. 3) strongly suggests a non-corner sharing type of binding.

Taking into account a larger range of 2.52–12.65 $Å^{-1}$, an additional Ti–Si distance of about 2.19 ± 0.05 Å was found to fit the data. This very short distance is compatible with an edge-sharing type of binding taking into account bond lengths of 1.65 ± 0.03 and 1.87 ± 0.02 Å for Si–O [24] and Ti–O as well as O–Si–O, O–Ti–O and Ti–O–Si angles of 118°, 104° and 69° ($\pm 3°$), respectively. Except for one example of SiO_2 allotropic form [24], this is the first evidence of such a binding. Other examples of this novel arrangement are being investigated for various coordination states of titanium [19]. A better fit quality is obtained when a titanium shell at about 2.6 Å is added (figs. 2a and 2b). Though statistically significant the signal to noise ratio does not allow a precise evaluation of the number of those neighbours; this shell probably accounts for dimeric sites.

The four shell (baseline residue, O, Si and Ti) simulations were based on the maximum of parameters that could be fitted independently. Such simulations do not satisfactorily account for the differences between the two samples as shown by the XANES analysis. A more complex environment is expected. Several attempts show that addition of a second shell of oxygen and silicon atoms at 1.92–2.16 and 2.8–3.1 Å, respectively, improved the fit. Though no accurate numbers can be obtained from such fits, some conclusion can be drawn. The

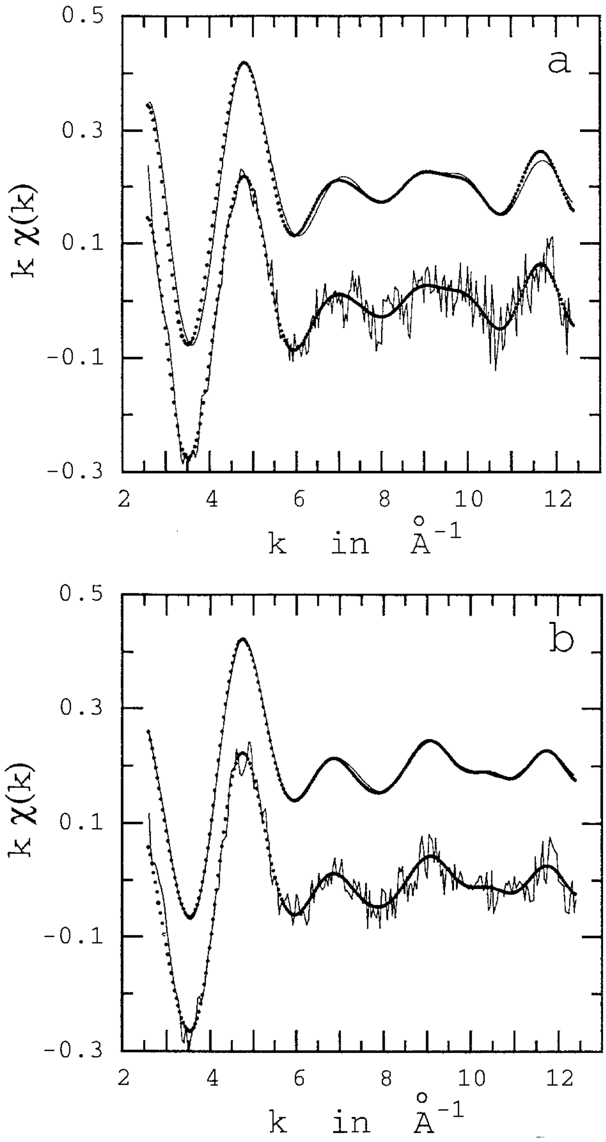


Fig. 2. Ti K-edge EXAFS oscillations of (a) 1.6-TS-2 and (b) 4.2-TS-2 samples: raw data (bottom, full line) with FT filter (between 0 and 2.85 Å, dots), four-shell simulation (top with a +0.2 offset, full line) with the FT filter (dots); (c) k^3 Fourier transforms of 1.6-TS-2 (top, +2.0 offset) and 4.2-TS-2 (bottom) filtered (dots) and simulated (full line).

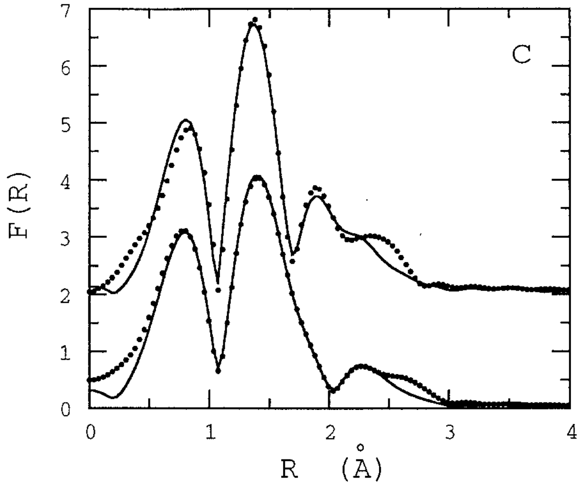


Fig. 2 (continued).

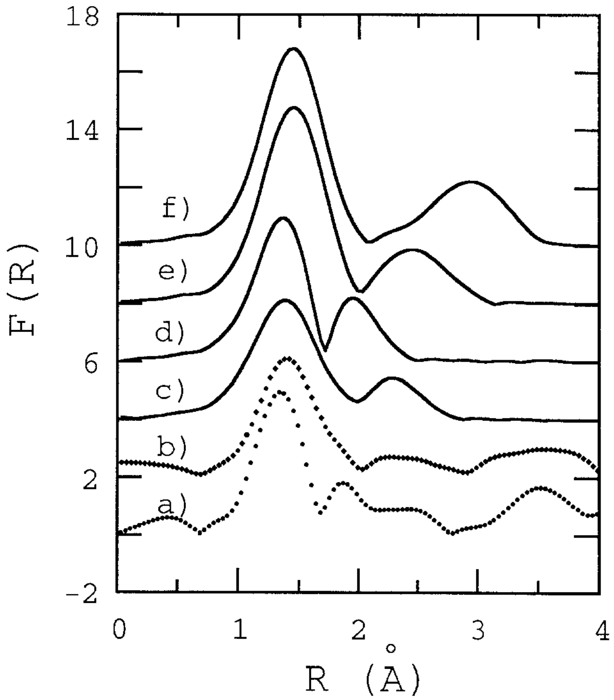


Fig. 3. EXAFS Fourier transform of the Ti K-edge of (a) 1.6-TS-2, (b) 4.2-TS-2 and simulated titanium in a (c) dimeric site (1 Ti at 2.60 Å), (d) monomeric tetrahedral site **3**, vicinal site **2** and (e) regular T site **1** (see, scheme of fig. 4; the multiscattering contribution ignored here would increase the Si FT peak of sites **2** and **3**).

Table 2
EXAFS simulation parameters for air exposed titanium silicalites

Ti/Ti+Si (%)	Simulation parameters [a]	Neighbours				
		O(1)	O(2)	Si(1)	Ti(1)	Si(2)
1.6 [b]	N	4.49 ± 0.71	–	1.98 ± 0.44	0.52 ± 0.37	–
	$\sigma \times 10^2$ (Å)	6.5 ± 1.6	–	4.0 ± 4.0	4.0 ± 4.4	–
	R (Å)	1.87 ± 0.02	–	2.20 ± 0.04	2.56 ± 0.05	–
	ΔE_0 (eV)	6.5 ± 1.5	–	-16.4 ± 6.9	-30 ± 40	–
4.2 [c]	N	3.93 ± 0.71	–	2.15 ± 0.62	0.50 ± 0.40	–
	$\sigma \times 10^2$ (Å)	5.5 ± 3.0	–	5.2 ± 4.1	4.0 ± 4.5	–
	R (Å)	1.88 ± 0.02	–	2.17 ± 0.026	2.54 ± 0.1	–
	ΔE_0 (eV)	7.5 ± 0.6	–	-19.9 ± 7.4	-25.8 ± 12.5 [d]	–
1.6 [d]	N	3.9	1.0	1.8	0.5	0.3
	R (Å)	1.87	2.02	2.19	2.60	3.0
4.2 [d]	N	3.6	1.4	1.4	0.7	0.5
	R (Å)	1.89	2.06	2.19	2.60	2.9

[a] N, σ, ΔE_0 and R are the numbers, Debye–Waller factor, energy threshold shift and distances of neighbouring atoms.

[b] The simulation was preformed in the 2.5–12.7 Å^{-1} range on a filter including the baseline residue (0–2.85 Å). There were eighteen independent parameters and the simulation was performed on seventeen parameters allowing a degree of freedom of 1. Fit quality χ^2/ν was equal to 0.88 with a residue of 4.8×10^{-3} (fig. 1).

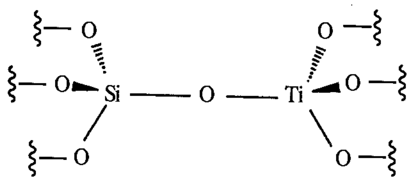
[c] As in b with a fit quality of 0.40 for a residue of 2.3×10^{-3} (fig. 1).

[d] Best fits with the additional spheres leading to a residue reduced by more than 2 times and fitting parameters very close for both samples with much less negative ΔE_0; for Si(1) and Ti(1), ΔE_0 falls in the -8 to -12 and -15 to -19 eV ranges (as for Ti and O backscatterers in anatase). Such substitutions of Si by Ti or O atoms were envisaged but did not lead to satisfactory fits neither to satisfactory realistic positions.

three shells first fitted are only slightly changed by the introduction of additional shells (table 2, bottom). For the higher Ti loaded silicalite the fit tolerates more titanium neighbours and more oxygen atoms at long distances. Furthermore, despite many attempts, an anatase-like environment was found unlikely to fit the data.

4. Discussion

Consistently with XANES results, EXAFS data are interpreted as the results of a mixture of, at least, two low coordination sites. None of them corresponds to expected site **1** or site **2** of fig. 4. The first one would be a monomeric species with four oxygens at short distances comparable to the tetrahedral sites with



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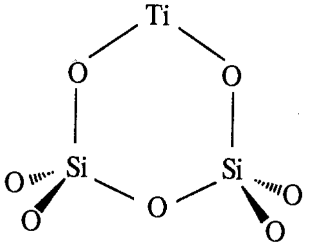

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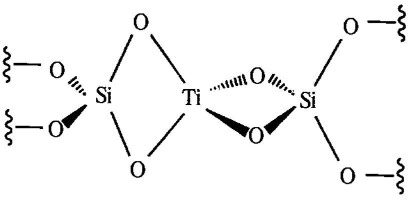

3

Fig. 4. Schematic representation of normal corner-sharing type of binding expected in a regular T site **1** (4 Si at about 3.44 Å) or in a site implying vicinal [SiO_4] units **2** (2 Si at about 3.0 Å) and novel edge sharing type of binding in a monomeric tetrahedral site **3** (4 Si expected at 2.25 Å).

Ti–O distances of 1.85 Å found in TiO_2–SiO_2 glasses [14]. Our data suggest that the monomeric site **3** necessitates two of the edge-sharing type of binding per titanium (fig. 4). The second site would be dimeric and seems to be more abundant in the 4.2-TS-2 sample. Its pre-edge peak intensity does not match the one of an octahedral site. This site is more likely pentacoordinated, either in a distorted trigonal bipyramid or, square pyramidal symmetry as previously proposed [10]. The pre-edge position at 3.0 eV is indeed intermediate between the positions associated to tetrahedral and pentacoordinated titanium (table 1). The particularly short Ti–Ti distance in comparison with the 3.0 ± 0.1 Å in oxides or coordination compounds [25,26] indicates a very strong stress in the "trapped" framework Ti pairs.

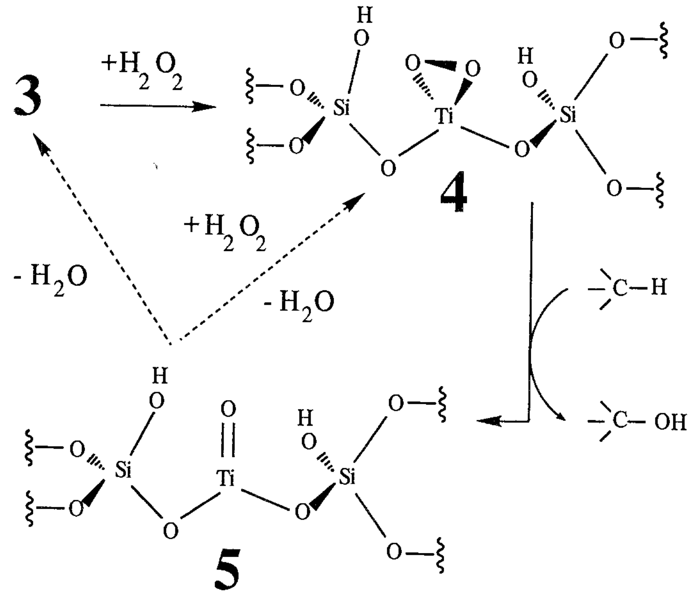

Fig. 5. Proposed oxyfunctionalization catalytic cycle with new site **3** including peroxotitanium(IV) **4** and titanyl **5** intermediates (broken line arrows indicate alternative routes).

The monomeric site **3** with this novel edge-sharing binding mode creates necessarily a local defect in the structure, i.e. within the framework or across a channel. From oxygen to oxygen atoms, this site is about 6.3 Å long and could indeed be sited from wall to wall across a framework channel which happens to be 5.8 Å wide in the Ti free MEL structure. If this is the case, the template molecule would imperfectly fit the obturated channel. Nevertheless, one cannot yet reject this hypothesis since the crystallinity was never found maximum when titanium was incorporated in the silicalite.

The IR band at 960 cm^{-1} could be associated to the SiO_4 unit double linked to a Ti ion. The disappearance of this band upon the action of hydrogen peroxide could be explained by the opening of the double μ-oxo bridge between the Ti and Si ions to form the peroxotitanium(IV) species **4**. Key intermediates including the titanyl species for the mechanism of oxyfunctionalization of alkanes [2,27] are compatible with the novel site structure as proposed in **4** and **5** (fig. 5). More investigations are in progress to further characterize the monomeric and the dimeric site. The latter could accomodate one shared edge with $[SiO_4]$ units as well as one Ti neighbour per titanium.

5. Conclusion

The titanium silicalite of ZSM-11 type of structure contains titanium monomeric sites where titanium is linked to the framework via a novel edge sharing type of binding. There are some evidences for dimeric sites as well. The similar structure, catalytic activity and recent EXAFS results for TS-1 [23] and TS-2 silicalites suggest that the titanium sites are similar for both materials, i.e. non-substitutional or framework defects.

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References

[1] M. Tamarasso, G. Perego and B. Notari, US Patent 4410501 (1983).
[2] D.R.C. Huybrechts, L. De Bruycker and P.A. Jacobs, Nature 345 (1990) 240.
[3] T. Tatsumi, M. Nakamura, S. Nagashi and H. Tominaga, J. Chem. Soc. Chem. Commun. (1990) 476.
[4] M.G. Clerici, G. Bellussi and U. Romano, J. Catal. 129 (1991) 159.
[5] J.S. Reddy, R. Kumar and P. Ratnasamy, Appl. Catal. 57 (1990) L1.
[6] B. Notari, Stud. Surf. Sci. Catal. 37 (1988) 413;
U. Romano, A. Esposito, F. Maspero, C. Neri and M.G. Clerici, Stud. Surf. Sci. Catal. 55 (1990) 33.
[7] M.R. Boccuti, K.M. Rao, A. Zecchina, G. Leofanti and G. Petrini, in: *Structure and Reactivity of Surfaces*, Vol. 48 (Elsevier, Amsterdam, 1990) p. 133.
[8] S. Kaliaguine, B. Nagy, Z. Gabelica, Stud. Surf. Sci. Catal. 35 (1988) 381.
[9] A. Lopez, H. Kessler, J.L. Guth, M.H. Tuilier and J.M. Popa, in: *Proc. 6th Int. Conf. X-ray Absorption Fine Structure*, York, 1990 (Elsevier, Amsterdam, 1990) p. 549.
[10] P. Behrens, J. Felsche, S. Vetter, G. Schulz-Ekloff, N.I. Jaeger and W. Niemann, J. Chem. Soc. Chem. Commun. (1991) 678.
[11] O. Clause, L. Bonneviot, M. Che and H. Dexpert, J. Catal. 130 (1991) 21.
[12] L. Bonneviot, O. Clause, M. Che, A. Manceau, D. Bazin and H. Dexpert, Catal. Today 6 (1989) 39.
[13] O. Clause, L. Bonneviot, M. Che, M. Verdaguer, D. Bazin and H. Dexpert, J. Chim. Phys. 86 (1989) 1767.
[14] B. Greegor, F.W. Lytle, D.R. Sandstrom, J. Wong and P. Schultz, J. Non Cryst. Solids 55 (1983) 27.
[15] A. Bittar, A. Sayari, D. Trong On, L. Bonneviot and S. Kaliaguine, in: *Proc. 6th Brazilian Cong. Catal.*, Salvador, 1991 (IBP/CAT, Rio de Janeiro, 1991) p. 567;
A. Bittar, D. Trong On, L. Bonneviot, S. Kaliaguine and A. Sayari, *Proc. IXth IZC*, Montreal 1992, in press;
D. Trong On, L. Bonneviot, A. Bittar, A. Sayari and S. Kaliaguine, J. Mol. Catal., in press.
[16] J.S. Reddy, R. Kumar and P. Ratnasamy, Appl. Catal. 58 (1990) L1;
J.R. Reddy and R. Kumar, J. Catal. 130 (1991) 440.
[17] G.T. Kokotailo, P. Chu, S.L. Lawton and W. Meier, Nature 275 (1978) 119.

[18] Reports on the International Workshops on Standard and Criteria in XAFS, in: *Proc. 6th Int. Conf. X-ray Absorption Fine Structure*, York, 1990 (Elsevier, Amsterdam, 1990) p. 751.

[19] A. Michalowicz, in: *Ecole du CNRS, Structures Fines d'Absorption en Chimie*, Garchy, September 1988 (CNRS, Paris, 1988).

[20] C.A. Yarker, P.A. Johnson, A.C. Wright, J. Wong, B. Greegor, F.W. Lytle and R.N. Sinclair, J. Non Cryst. Solids 79 (1986) 117.

[21] B.K. Teo, in: *EXAFS: Basic Principles and Data Analysis* (Springer, Berlin, 1986) pp. 45,89.

[22] A.G. McKale, B.W. Veal, A.P. Paulikas, S.-K. Chan and G.S. Knapp, J. Am. Chem. Soc. 110 (1988) 3763.

[23] L. Bonneviot, unpublished.

[24] F. Liebau, in: *Structural Chemistry of Silicates* (Springer, Berlin, 1985) pp. 13, 93.

[25] T.V. Lubben and P.T. Wolczanski, J. Am. Chem. Soc. 109 (1987) 424.

[26] I.D. Williams, S.F. Pedersen, K.B. Sharpless and S.J. Lippard, J. Am. Chem. Soc. 106 (1984) 6430.

[27] D.R.C. Huybrechts, I. Vaesen, H.X. Li and P.A. Jacobs, Catal. Lett. 8 (1991) 237.

[28] F. Babonneau, S. Doeuff, A. Leaustic, C. Sanchez, C. Cartier and M. Verdaguer, Inorg. Chem. 27 (1988) 3166.