In situ XANES studies of Titanium sites and their reactivities in nanoporous Titanosilicate frameworks

Nguyen Khanh Dieu Hong
Hanoi University of Science and Technology
Vo Duc Anh, Nguyen Thi Ha
Ho Chi Minh University of Industry
Richard A. Catlow
Department of Chemistry - University College London

Abstract

This study focused on the study of titanium sites, their local structure and reactivities in nanoporous titanosilicates frameworks by using in situ X-ray absorption spectroscopy. XANES provide the information on the oxidation state of the titanium species as well as their change in coordination geometry during de- and re-hydration. Results from in situ XANES studies shows that TS-1 is much more hydrophobic than TiAl or TiFe systems. Pre-edge features of Ti K-edge XANES spectra of these materials also suggested that Ti^{IV} is the dominant Ti coordination in dehydrated system whilst Ti^{VI} is the dominant in the re-hydrated one.

1. Introduction

Titanium-containing nanoporous materials attract much interest because of their remarkable catalytic properties in various oxidation reactions. Titanosilicate materials are shown to catalyze oxidation reactions in the presence of hydrogen peroxide H_2O_2 (as an oxidant) where only water is given off as the by-product. Therefore such materials act as catalysts in 'green' reaction systems. Some of the applications of these catalyst are for the epoxidation of cyclohexene to form epoxides [1, 2, 3]; the catalytic oxidation of propylene to propylene oxide [4].

TS-1, a member of the titanosilicate, family represented by the MFI structure-type has been investigated intensively because of its particularly high catalytic activity which likely derives from its high surface hydrophobicity. This feature means that the adsorption of the organic substrates are more favoured over more polar species such as water since the organic molecules are kept in the pores near Ti^{IV} sites.

During the 1980s, it was proposed that titanium in the TS-1 catalyst was present as titanyl groups or as the corresponding hydrated system [5]. Later, in 1993, this model was corrected using EXAFS measurements to interpret the nature of the titanium species [6]. It was reported that titanium sites are Ti^{IV} in the calcined framework. XANES/EXAFS spectroscopy has been used ever since in view of the fact that it gives direct proof of the coordination of titanium sites in a system [7].

Further studies on the Ti-containing catalyst using X-ray absorption, UV-VIS, IR spectroscopy and computational work [8, 9] yield evidence that Ti^{IV} resides in tetrahedral coordination in the calcined TS-1. Although this structural model for the active site is accepted, there are several issues constantly reported in the literature. For example, Sankar, Catlow and Thomas [10] reported that the titanium in tetrahedral coordination in TS-1, Ti-zeolite b and Ti-MCM-41 but the pre-edge intensity is not the same in all these catalysts. A possible explanation given for this difference may be related to the nature of distortion in the tetrahedral geometry which may affect the pre-edge intensities.

In 1996, F. Farges et al [11] suggested that pre-edge position and height of Ti K-edge XAFS spectra can be used to derive accurate information on the local coordination environment of Ti sites. Using these features, it is possible to distinguish between one coordination environment vs. a mixture of several others. In their work, Ti K-edge spectra were collected for several model compounds in which Ti is located in 4-, 5- or 6-coordinated sites: Ti^{IV}(as Y_2TiMo_8); Ti^{V}(as $K_2Ti_2O_5$) and Ti^{VI} (as $CaTiSiO_5$). Their study indicated that the use of both position and height of the pre-edge is required to extract reliable Ti coordination numbers from pre-edge features in Ti-XANES spectra of examined materials.

This work presents the study of titanium sites and their reactivity in some nanoporous frameworks with MFI structure. In particular, *in situ* X-ray absorption spectroscopy, XAS, was employed to investigate the local structure around the active titanium sites during de- and re-hydration process. The intensity (height) and position of the pre-edge peak, which is related to the coordination geometry of titanium sites is extensively used in this study. Furthermore we highlight and compare local environments and reactivities of titanium sites in titanium-cogel precursors (used to prepare TS-1 catalysts), titanosilicate (TS-1) and multi-metallosilicate (MTS-1, where M=Fe or Al) hosts.

2. Experimental

2.1. Model compounds for XANES studies

In this work three model compounds for XAS measurement were used: ETS-10, Fresnoite ($Sr_2TiSi_2O_8$) and $Ti(OSiPh_3)_4$. The reason being, all these materials have identical first and second neighbour atoms similar to the one that is present in titanosilicates.

The structure of three model compounds and suggested models of coexisting titanium sites in the materials examined in this studies are co-plotted in Fig. 1 (a, b, c, d, e). The suggested models of titanium sites in examined titanosilicates will be confirmed in the results and dicussion. XANES spectra of three model compounds are also presented in Fig. 17.

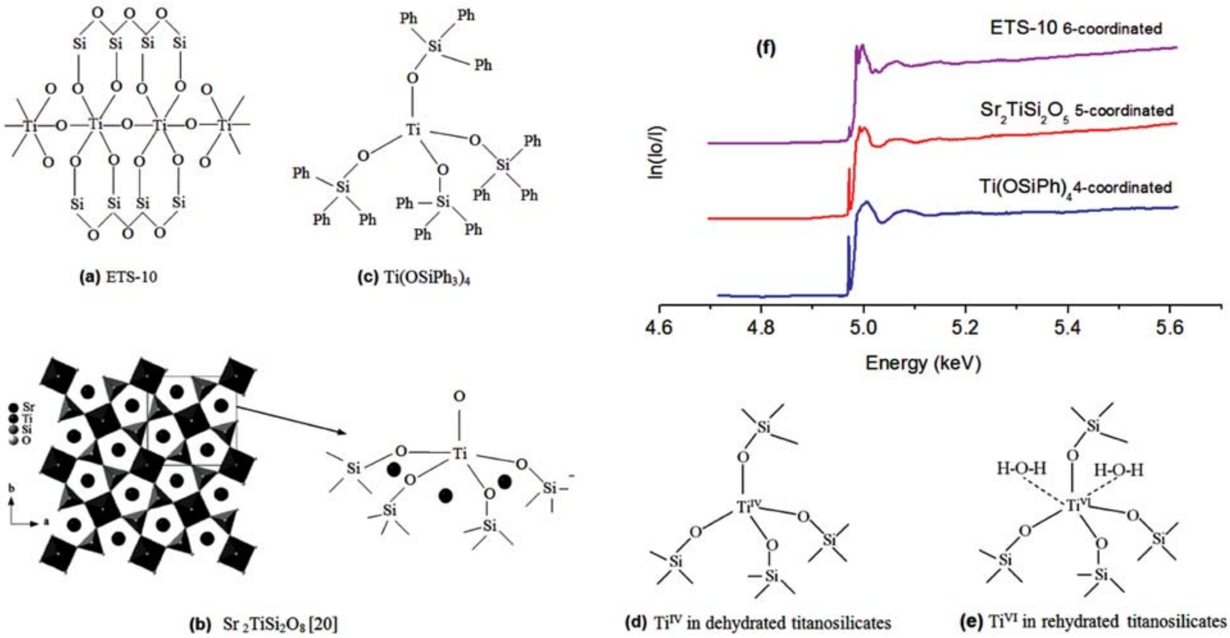
ETS-10 is a large pore nanoporous zeotype material, consists of corner-sharing TiO_6 and SiO_4 linked together through bridging oxygen atoms (Fig. 1a) [8, 9]. The crystal structure of Fresnoite, $Sr_2TiSi_2O_8$ possesses an interesting peculiarity as it is one of the few instances of five-fold co-ordinated titanium located inside a square pyramid [12]. $Ti(OSiPh_3)_4$ is a four-coordinate, tetrahedral and monomeric compound in which Ti^{IV} sites are shrouded by the bulky triphenyl groups [13] (Fig. 1c).

XANES examinations reported in this paper were all recorded at station BM26, ESRF, Grenoble, France.

2.2. *In situ* XANES set up

Fig. 2 shows schematic representation of the calcination cell used to obtain XANES spectra of the de/re-hydrated materials examined.

In an typical experiment, a 100mg of the catalyst disc of 20mm diameter was mounted into the quartz sample holder. Materials were then heated to 400°C at 5°C/min in dry air. Following this, samples were then cooled to room temperature. During measuring the Ti K-edge XAS,



(a) ETS-10 **(c)** $Ti(OSiPh_3)_4$

(b) $Sr_2TiSi_2O_8$ [20] **(d)** Ti^{IV} in dehydrated titanosilicates **(e)** Ti^{VI} in rehydrated titanosilicates

Fig. 1. *Structure of three model compounds containing Ti^{IV}, Ti^{V}, Ti^{VI} coordination and suggested models of titanium sites co-exist in the materials examined are co-plotted with XANES spectra*

water vapour was prior introduced into the cell through a bubbler for re-hydration studies, which will represent the reactivity during catalysis, since hydrogen perioxide typically used contains about 70 percent water.

X-ray diffraction measurements were collected on a Siemens D500 diffractometer at University College London.

2.3. Nanoporous titano silicate materials preparation

All titanosilicate and metallosilicate samples in this work were synthesized from the cogel precursors by Amber Welch and was reported in ref [2].

First, the cogel precursor was prepared. Tetraethylorthosilicate (TEOS) (98%, 49.8g, 0.2mol) was slowly added to a stirred solution of distilled water (20.0g, 1.1mol) and dilute hydrochloric acid (0.1M, 20.0g, 0.5mol) and the resultant solution stirred for 45 minutes. A separate solution of the heteroatom source* in isopropyl alcohol (110.0g, 1.8mol), was vigorously stirred for ~ 4 hours. The two solutions were then mixed and further agitated* whilst an aqueous solution of ammonium salt* was added drop wise until gelation occurred. The transparent white gel was then dried overnight ~ 80°C, calcined (if required) (3°C min^{-1} to 535°C, 4 hours maintained) crushed and the resultant white powder (~ 40.0g) stored under ambient conditions.

The SiO_2-TiO_2 cogels were prepared using the sol-gel process which gives control over both the properties and chemical composition of the raw material. In the TS-1 cogel, the titanium and silicon atoms are bound through oxygen bridges, stabilising the titanium atoms and preventing TiO_2 precipitation during the synthesis procedure [10, 11]. The prepared cogel precursor was converted into Ti-S1 by reacting with tetrapropylammonium hydroxide, under hydrothermal conditions.

Similarly, the multi-heteroatom cogels for the synthesis of multi-metallosilicate were prepared from two separate sources of heteroatoms. S1 was used as the suffix for framework materials additionally specific nomenclature was adopted that would make the nature of the heteroatoms easily explicable. MFI materials with incorporated titanium and aluminium/iron centres were named TiAl-S1 and TiFe-S1. For each system, we have also examined their cogel precursors.

3. Results and discussion

XRD pattern of all calcined cogels (cogels were calcined at the rate 3°C min^{-1} to 535°C, 4 hours maintained) and as-synthesized materials were shown in Fig. 3. As is clearly visible, the cogel appears amorphous with no long-range order. Conversely, the as-prepared Titanosilicate materials show a crystalline nature and adopt the framework type of MFI.

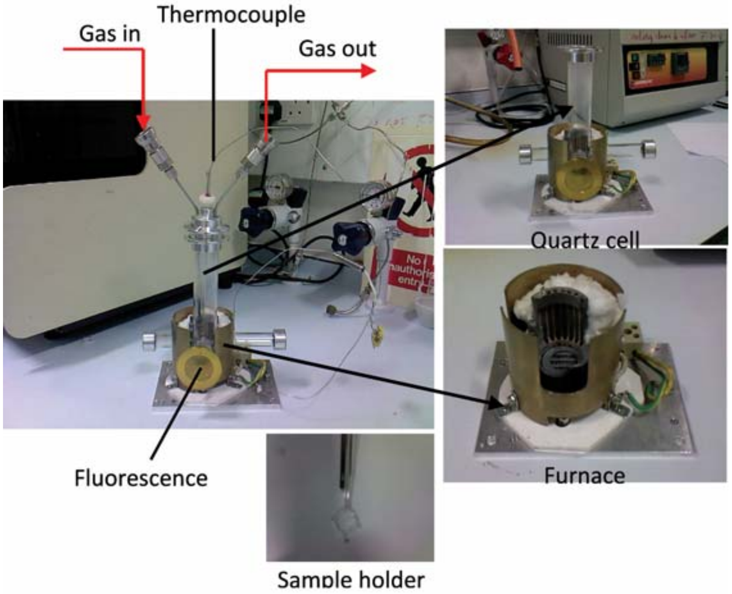


Fig. 2. *Schematic representation of the calcination cell used to obtain XANES spectra of the de/re-hydrated materials*

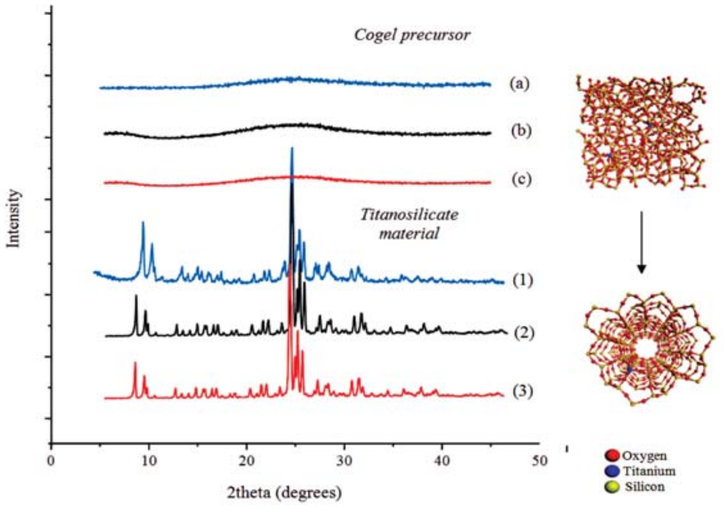


Fig. 3. *XRD pattern of all calcined cogels and as-synthesized Titanosilicate materials (1, a): TS-1 and TS-1 cogel; (2, b): TiAl-S1 and TiAl cogel; (3, c): TiFe-S1 and TiFe cogel*

3.1. XANES studies of model compounds

XANES features of model compounds are shown in Table 1.

The XANES spectrum of ETS-10, in which titanium is in octahedral coordination, has a pre-edge intensity of 0.19926 and position at 4.97208keV (4972.08eV). The XANES spectrum of $Sr_2TiSi_2O_8$ material, a model compound for Ti sites in pentahedral coordination, has a pre-edge at 4.7128keV with intensity of 0.56776. The $Ti(OSiPh_3)_4$ material, which is a model compound for Ti sites in tetrahedral coordination, has a pre-edge intensity of 0.87399. Its pre-edge position is at the lower energy of 4.97068keV (4970.68keV).

Direct correlation between the pre-edge position of a sample and its intensity can be established from Table 1: tetrahedrally coordinated systems have a higher pre-edge intensity, which appears at a lower energy than that of an octahedrally coordinated titanium site as we have confirmed in Fig. 1. Pentahedrally coordinated systems have a pre-edge intensity and location in between tetrahedrally and octahedrally coordinated systems.

3.2. Study of Ti sites in TS-1 system

3.2.1. XANES study of titanium-cogel

Pre-edge of Ti K-edge XANES of the Ti-cogel and TS-1 recorded during an *in situ* study are plotted in Fig. 4, in which: (A): up on the calcination up to 400°C, (B): upon the re-hydration, (C): complete plot of Pre-edge of Ti K edge XANES and (D): pre-edge intensity vs energy positions compared with the model compounds.

As seen in Fig. 4 (left), the intensity of pre-edge in XANES of Ti cogel increased upon increasing the temperature of de-hydration to 400°C (a) and decreased upon the re-hydration (b), suggesting a change in the local environment of the Ti sites in the system during these processes. As-prepared cogel has a pre-edge intensity of 0.3245 and its position appeared at 4.97094keV. After de-hydration to 400°C, the pre-edge shifted towards lower energy values, specifically, 4.97071keV, and its intensity reached 0.79145.

In the following step, the sample was then cooled down and water was introduced into the system. After re-hydration, the pre-edge intensity decreased to 0.26375 and the position of pre-edge peaks shifted back to a higher energy of 4.97154keV.

It is clear from Fig. 4D (left), all as-prepared/de-hydrated/re-hydrated samples have a lower pre-edge intensity compared with the model compound $Ti(OSiPh_3)_4$ and a higher pre-edge intensity compared with that of ETS-10. Pre-edge position of all samples are between $Ti(OSiPh_3)_4$ and ETS-10. From comparison with pre-edge feature of $Sr_2TiSi_2O_8$, it is inferred that the titanium centres of prepared cogel contains a mixture of tetrahedral and octahedral coordination rather than a pentahedral one. The pre-edge position is more similar to that for a tetrahedral system (with dehydrated material) and for octahedral system (with hydrated material) than for a pentahedral one. The pre-edge intensities of the re-hydrated Ti-cogel are much lower than that of the de-hydrated one. This suggests that water interacts with Ti^{IV} sites upon exposure to atmosphere. However the re-hydrated Ti-cogel does not generate the type of octahedral coordination seen for ETS-10.

3.2.2. XANES study of TS-1

As noted in the XANES study of the Ti-cogel, TS-1 shows a lower pre-edge intensity compared with the de-hydrated material, and the model compound, $Ti(OSiPh_3)_4$ (Fig. 5D right). This suggests that water interacts with Ti^{IV} centres upon exposure to the atmosphere. As-prepared TS-1 has a pre-edge intensity of 0.3481 and its position at 4.97094keV. After de-hydration to 400°C, the pre-edge shifted towards lower energy to the value of 4.97068keV, and its intensity reached 0.52323.

After cooling and re-hydration the pre-edge intensity decreased to 0.2342 and the position of the pre-edge peaks shifted back to a higher energy of 4.97134keV. This reactivity of pre-edge in XANES of TS-1 is found to be very similar to the reactivity of the pre-edge of the Ti-cogel precursor.

Although the pre-edge in XANES of the as-prepared TS-1 appeared at the same energy as the cogel precursor, their pre-edge intensity is different. The pre-edge intensity in XANES of the as-synthesized TS-1 (0.3481) is higher than that in the prepared co-gel (0.3245).

Table 1. *Ti K-edge XANES features of three model compounds*

Model compound	Pre-edge intensity	Pre-edge position, keV
Ti^{VI}-ETS-10	0.19926	4.97208
Ti^{V}-$Sr_2TiSi_2O_8$	0.56776	4.97128
Ti^{IV}-$Ti(OSiPh_3)_4$	0.87399	4.97068

Pre-edge features of TS-1 and Ti-cogel, compared with three model compounds, shows that both cogel precursor and as-synthesized materials contain a mixture of Ti^{IV} and Ti^{VI}. However, octahedral coordination generated by the interaction of water molecules with titanium centres does not generate the same octahedral coordination seen the in ETS-10 model compound.

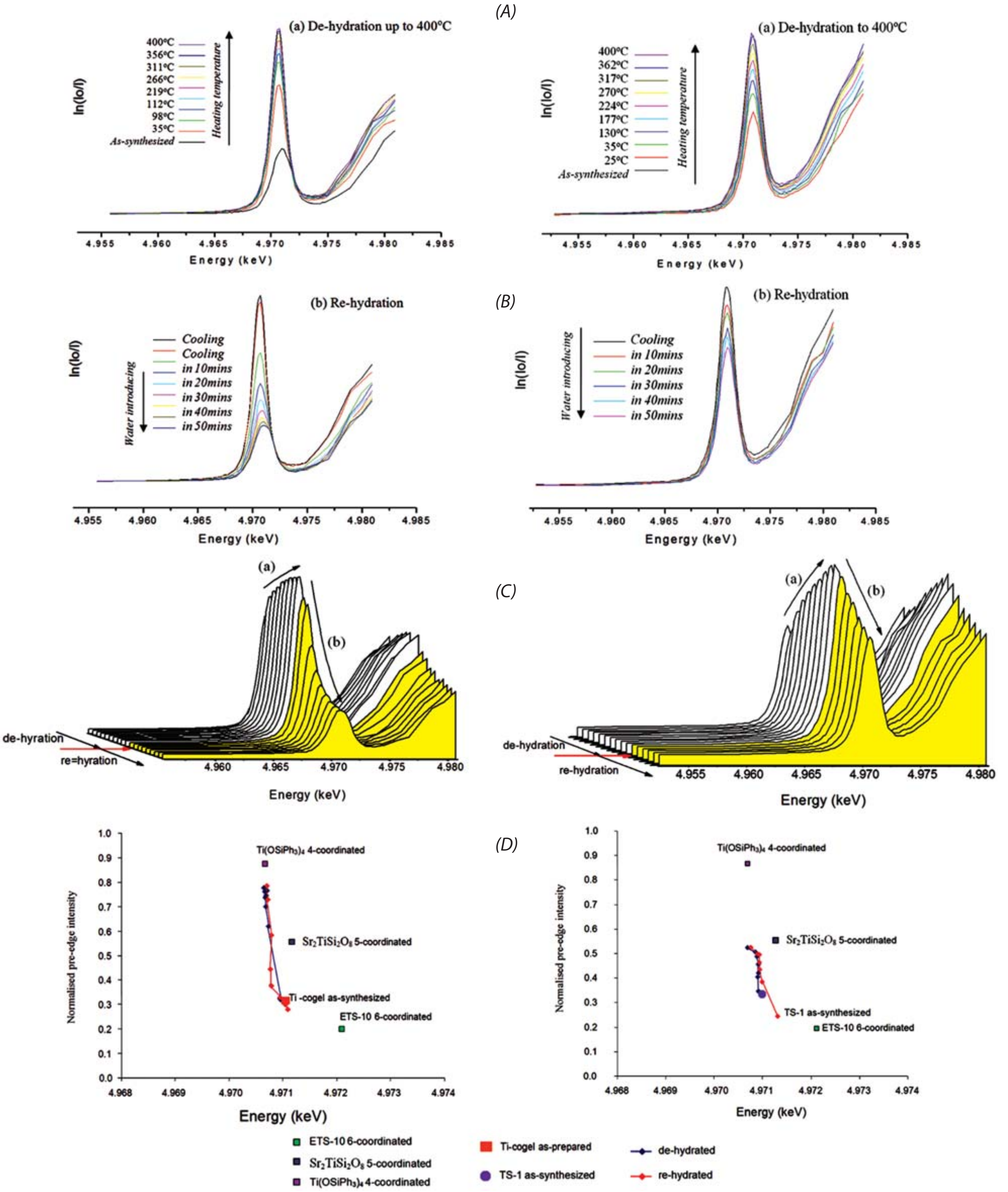


Fig. 4. *Pre-edge studies of Ti K-edge XANES of the Ti-cogel (left) and TS-1 (right) recorded during an in situ study upon the calcination and re-hydration*

***Table 2.** Ti K-edge XANES features of TiAl-cogel and TiAl-S1*

Pre-edge features	**TiAl-cogel sample**			**TiAl-S1 sample**		
	Before dehydration (As-prepared)	At 400°C	After rehydration	Before dehydration (As-prepared)	At 400°C	After rehydration
Pre-edge intensity	0.23746	0.68765	0.21223	0.36777	0.65081	0.42178
Pre-edge position, keV	4.97134	4.97054	4.97134	4.97114	4.97054	4.97074

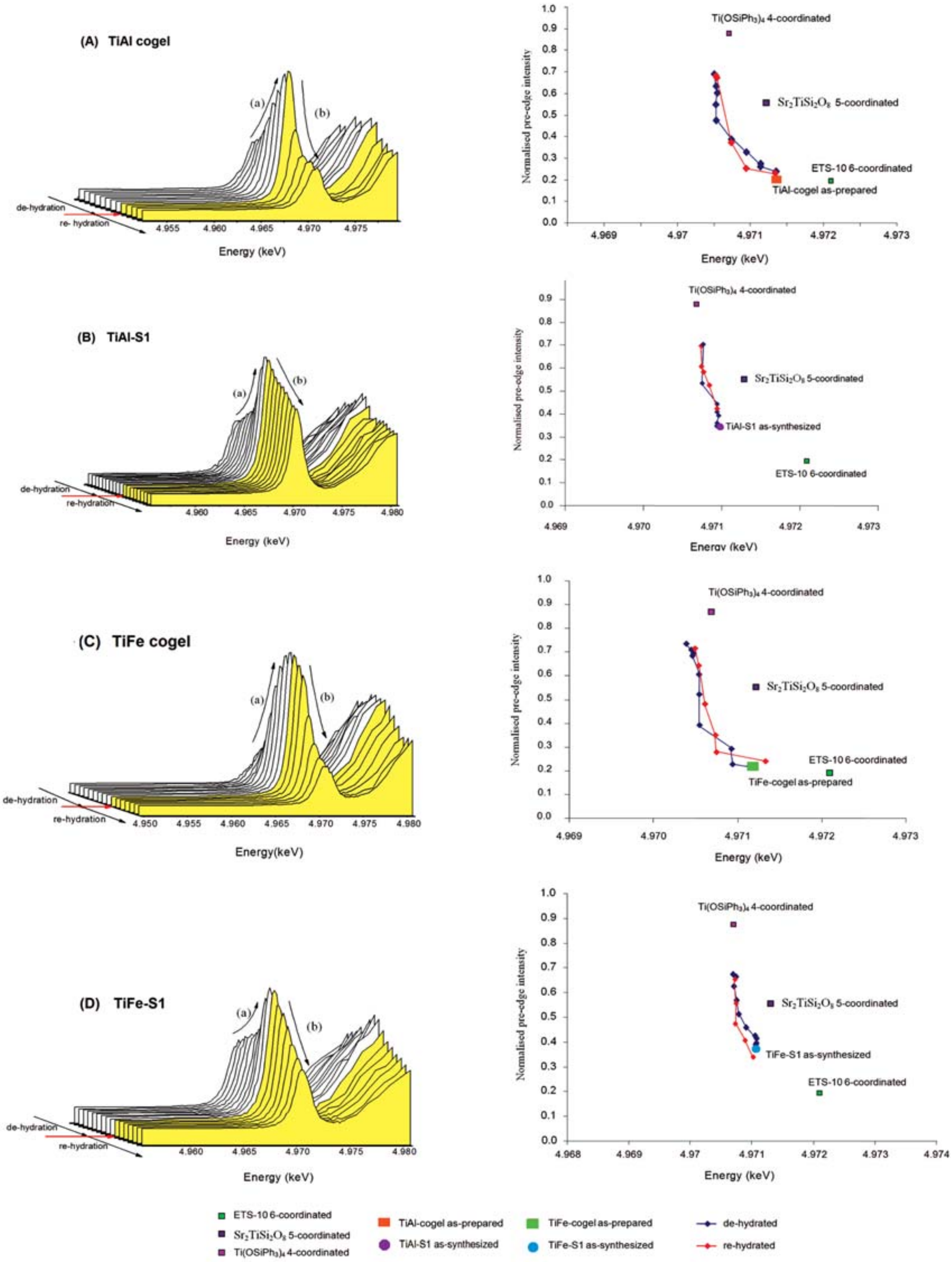


***Fig. 5.** Pre-edge studies of Ti K-edge XANES of (A): TiAl cogel, (B): TiAl-S1, (C): TiFe-cogel; (D) TiFe-S1 recorded during an in situ study upon the calcination and re-hydration*

3.3. Study of Ti sites in TiAl-S1 system

3.3. 1. XANES study of TiAl-cogel

Pre-edge of Ti K edge XANES of the TiAl-cogel, TiAl-S1 and TiFe-cogel, TiFe-S1 (will be discussed in 3.3) are co-plotted in Fig. 5, in which on the left is the complete plot of Pre-edge of Ti K edge XANES and on the right is the pre-edge intensity vs energy positions compared with the model compounds.

As seen in Fig. 5A and Table 2, the intensity of the XANES pre-edge of the TiAl-cogel, similarly to Ti-cogel, increased upon the de-hydration to 400°C (a) and decreased upon re-hydration (b) with the pre-edge intensity shifted back to a higher energy, showing the changing local environment of Ti sites in the system.

Pre-edge intensities of the re-hydrated TiAl-cogel are much lower than that of the de-hydrated one. Compared with model compound $Ti(OSiPh_3)_4$, all as-prepared/re-hydrated sample have a lower pre-edge intensity. However the position of the pre-edge of the de-hydrated sample is identical to that of $Ti(OSiPh_3)_4$ and is at much lower energy compared with ETS-10. Upon exposure to atmosphere, the decrease in pre-edge intensity of the XANES clearly indicates that water molecules interact with the titanium centre yielding a distorted octahedral coordination. However, this distorted octahedral coordination is not like the octahedral coordination generated in ETS-10 system.

The reactivity of pre-edge peak in TiAl-cogel XANES spectrum showed that prior to crystallisation, the cogel contained a mixture of Ti^{IV} and Ti^{VI} geometry

3.3.2. XANES study of TiAl-S1

As-prepared TiAl-S1 K-edge has a very similar behavior with TS-1, showing that de-hydrated TiAl-S1 contain Ti^{IV}. After the calcinations, tetrahedral titanium centres are produced in the system. Upon exposure to the atmosphere, the decrease in pre-edge intensity of the XANES clearly indicates that water molecules interact with the titanium centre yielding a distorted octahedral coordination. However, this distorted octahedral coordination is not like the octahedral coordination generated in ETS-10 system.

Compared with pre-edge feature of $Ba_2TiSi_2O_8$, this suggests that the titanium centres of TiAl-S1 are in a mixture of tetrahedral and octahedral coordination rather than a pentahedral one. The pre-edge position in XANES spectra of TiAl-S1 is more similar to that for a tetrahedral system (with dehydrated material) and for octahedral system (with hydrated material) than for a pentahedral one.

3.4. Study of Ti sites in TiFe-S1 system

3.4.1. XANES study of TiFe-cogel

As shown in Fig. 5C and Table 3 the intensity of pre-edge in XANES of the TiFe-cogel increased upon the increasing temperature of de-hydration to 400°C and decreased upon the re-hydration.

Compared with three model compounds, it can be confirmed that prior to crystallisation, the TiFe-cogel has contained a mixture of titanium sites of Ti^{IV} and Ti^{VI} coordination geometry.

3.4.2. XANES study of TiFe-S1 system

From Table 3 and Fig. 5D, this reactivity shows that the Ti^{IV} sites in the de-hydrated system changed to distorted octahedral after the re-hydration.

It can be seen clearly that the pre-edge intensities of the as-prepared/re-hydrated TiFe-S1 are much lower than that of the de-hydrated one showing two different type of coordination. There is a significant difference between the pre-edge intensity of as-prepared/re-hydrated materials with model compound $Ti(OSiPh_3)_4$. The re-hydrated samples have a much lower pre-edge intensity than $Ti(OSiPh_3)_4$ but the intensities are close to pre-edge intensity of ETS-10, suggesting that this material generated a distorted octahedral coordination of titanium sites. However, it does not generate the type of octahedral coordination seen for ETS-10 as its pre-edge energy is lower.

Table 3. *Ti K-edge XANES features of TiFe-cogel and TiFe-S1*

Pre-edge features	**TiFe-cogel sample**			**TiFe-S1 sample**		
	Before dehydration (As-prepared)	At 400°C	After rehydration	Before dehydration (As-prepared)	At 400°C	After rehydration
Pre-edge intensity	0.22444	0.72053	0.23855	0.37993	0.66227	0.34324
Pre-edge position, keV	4.97114	4.97054	4.97134	4.97114	4.97074	4.97094

4. Conclusion

XANES study of all cogel precursors and as-synthesized/de-hydrated MFI materials can be rationalized by considering that titanium in all these materials exist in a mixture of two types of coordination geometry. One type of site is tetrahedral and inaccessible to water molecules (hydrophobic). The other type of site is distorted octahedral containing four oxygens of the framework and two oxygens from water molecules (hydrophilic sites). This octahedral environment is different from that of Ti sites generated in ETS-10 model compound (Fig. 1). Pre-edge features of Ti K-edge XANES spectra of these materials suggest that Ti^{IV} is the dominant Ti coordination in dehydrated system whilst Ti^{VI} is dominant in the re-hydrated one.

The reactivity of pre-edge features (positions and heights) upon de/re-hydration can be explained by numbers of tetrahedrally/octahedrally coordinated titanium sites in the mixture. Upon dehydration, two loosely bound water molecules are desorbed from octahedrally coordinated titanium leading to a lower number of hydrophilic sites. As a result, the pre-edge intensity is higher and more similar to that for a tetrahedral system. In re-hydrated samples, when we have a higher number of hydrophilic sites, the pre-edge intensity is lower and more similar to that for an octahedral system.

One of the main conclusions that may be derived based on this study is that, TS-1 is much more hydrophobic than TiAl or TiFe systems. In particular uptake of water appears to indicate that titanium ions are more hydrophilic in these systems. This may have relevance in designing catalytic reactions. Welch [2] showed in her work that TS-1 has more selectivity towards epoxide formation compared to either co-gel or TiAl or TiFe systems. This implies that more the hydrophilic character are present in the other systems and hence further break down of epoxide to diol and other by-products which are catalysed by weak acid sites. Further work, in particular during "actual catalytic reactions" is needed to further confirm these results.

More importantly, this study, once again, re-confirms the sensitivity of pre-edge in XANES with the changing of local environment of metal sites in nanoporous materials.

Acknowledgement

Hanoi University of Science and Technology, Royal Institution of Great Britain, University College London are acknowledged for encouragement and financial support.

References

1. C. Zenonos. *Synthesis and Characterization of metal substituted microporous materials*. Doctoral thesis. Royal Institution of GB. 2003.

2. A. Welch. *Doctoral thesis*. Royal Institution of GB. 2007.

3. R. A. Sheldon, I. W. C. E. Arends, and H. E. B. Lempers. *Collection of Czechoslovak Chemical Communications*. 1998; 68: P. 1724.

4. J. M. Thomas and G. Sankar. *Journal of Synchrotron Radiation*. 2001; 8: p. 55.

5. R. A. Sheldon. *Journal of Molecular Catalysis*. 1983; 20 (1): p. 1.

6. L. Bonneviot, D. T. On, and A. Lopez. *Journal of the Chemical Society - Chemical Communication*. 1993; 8: p. 685.

7. F. Farges, G. E. Brown JR., A. Navrotsky, H. Gan and John J. R. *Geochimica et Cosmochimica Acta*. 1996; Vol. 60 (16): p. 3039.

8. A. Eldewik, Russell F. Howe. *Microporous and Mesoporous Materials*. 2001; 48: p. 65.

9. Y. K. Krisnandi, P. D. Southon, A. A. Adesina and Russell F. Howe. *International Journal of Photoenergy*. 2003; Vol. 5: p. 131.

10. C.M. Barker, D. Gleeson, N. Kaltsoyannis, C.R.A. Catlow, G.Sankar and J.M. Thomas. *Physical Chemistry Chemical Physics*. 2002; 4 (7): p. 1228.

11. F. Farges, G. E. Brown JR. and John J. R. *Geochimica et Cosmochimica Acta*. 1996; Vol. 60 (16): p. 3023.

12. G. Perego, G. Bellusi, C. Corno, M. Tarramaso, F. Buonomo, and E. Esposito. *Studies in Surface Science and Catalysis*. 1986; 29: p. 129.

13. B. F. G. Johnson, M. C. Klunduka, C. M. Martina, G. Sankar, S. J. Teatec and J. M. Thomas. *Journal of Organometallic Chemistry*. 2000; 596 (1 - 2): p. 221.