Small-angle X-ray scattering documents the growth of metal-organic frameworks

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1. Introduction

Metal organic frameworks (MOFs) are porous coordination polymers built up by bridging ligands that coordinate to metal ions or clusters. The high stability of some MOFs combined with a large degree of structural and chemical versatility makes them attractive for a number of applications, such as separation [1–5], gas storage [6–10], catalysis [11–15], drug-delivery [16–20], luminescence [21–25] and magnetism [26–30].

Although reports on coordination polymers go back to the 1960s, it was only after Robson and Hoskins re-discovered and boosted the field in 1989 [31] when coordination polymers rapidly developed, with reports on MOFs with very large surface areas, uncoordinated metal sites, and sometimes exceptionally high chemical and thermal stabilities [32–39].

Although a certain extent of control over MOF formation is claimed and the terminology of ‘building units design’ and ‘reticular synthesis’ were coined at the beginning of this century, unpredictability in synthesis does play a role, and it would not be overly controversial to state that several new topologies have been discovered by fortune rather than by design [36,40,41]. As the mechanism of crystallization is of utmost importance to crystal engineering and to the application of these materials in tools and devices, understanding crystallization becomes a very important matter.

Scattering techniques are capable of providing detailed information about in situ crystal growth and nucleation, and information from nano- to microscale about size and morphology. The most powerful scattering techniques are small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS). SAXS provides high-resolution scattering profiles for systems and events occurring at a wide scale range (1–200 nm). Moreover, simultaneous recording of scattering at small and wide angles (SAXS/WAXS) is possible by using multiple detectors. The formation and morphology of particles or crystals, i.e., scattering entities, can be investigated by SAXS, and their crystalline properties by WAXS, both in a time-resolved fashion.

Although the number of SAXS based studies on MOFs is small, interesting investigations have been published in recent years. Tsao et al. were the first to apply SAXS for the study of MOF systems, more specifically, MOF-5, mainly providing detailed nanostructural information about the material [42,43]. Topological information, in line with the work of Tsao was presented by Klimekow et al. on mechanosynthesis; they extended structural analysis with qualitative use of SAXS [44].
In attempt at resolving the mechanism of MOF growth, which is also the scope of this work, three papers using in situ SAXS have been recently published. Cravillon et al. studied the formation of ZIF-8 to obtain time-resolved structural information and demonstrated that nucleation governs the growth of this material [45]. In similar fashion, our group modelled the kinetics for the competitive growth between two frameworks built up by identical precursors: NH2-MIL-53(Al) and NH2-MIL-101(Al) (see Fig. 1) [46], in which the former is the thermodynamic product and the latter the kinetic product. In addition, the templation effect on MOF growth by phosphotungstic acid, one of the best-known Keggin-type polyoxometalates, were revealed [47]. Molecular-scale effects, events and growth of MOFs were also revealed through use of other synchrotron-based techniques, energy dispersive X-ray diffraction (EDXRD) and X-ray absorption spectroscopy, as published by Walton et al. [48–53].

NH2-MIL-53(Al) and NH2-MIL-101(Al) are two MOFs with outstanding adsorptive, catalytic and optical properties [54–63]. NH2-MIL-53(Al) with chemical formula Al( OH)2O2C–C6H5–NH2–CO2 is similar to the unfunctionalized MIL-53 structure, is built up by from diamond-shaped channels and is the only product when pure water is the solvent of synthesis. NH2-MIL-101(Al) is a mesoporous framework with a MTN topology and formula Al6(O)4[DMF]12(O2C–C6H5–NH2–CO2)3. Although both MOFs grow from the same precursors, the aluminium coordination is different [38,61]. In the case of MIL-53 Al ions are linked by μ2-OH bridges that yield 1D chains, whereas for MIL-101 μ3-O bridges link three ions at once, forming a trimeric secondary building unit (SBU) (see Fig. 1) [38].

In this work, we present a thorough analysis of previous and newly collected in situ SAXS/WAXS data collected during the crystallization of NH2-MIL-101(Al) and NH2-MIL-53(Al). The formation of MOF precursors and their transformation to small MOF crystals is studied in detail at a length scale of the order 1–70 nm. Several parameters are determined describing particle morphology, i.e. radius of Gyration, Porod volume and surface-volume as a function of time, demonstrating that crystallization of two phases follows very different chemical and morphological pathways.

2. Experimental

Aluminium chloride (AlCl3·6H2O, Fluka, purum p.a.), 2-aminoterephthalic acid (Aldrich, 99%) and DMF (Sigma, 99.8% anhydrous) were used as received. Metal and organic precursors were first dissolved in DMF or water and then the solutions were mixed. Synthesis solutions were prepared with the ratios depicted in Table 1. After vigorous stirring for 5 min, 0.1 m aliquot was transferred to the in situ cell.

A specially designed synthesis cell was used for the experiments (Fig. 1). The synthesis solution was loaded between two mica windows (10 mm windows, 50–100 μm thickness) separated by PTFE spacers (1.5 mm thickness). Heating was provided by four

![Fig. 1. MOF structures under study: in NH2-MIL-53(Al) Al ions are linked by μ2-OH bridges that yield 1D chains. In NH2-MIL-101, μ3-O bridges form a trimeric secondary building unit (SBU). NH2-MOF-235(Al) is built up from the same trimeric μ3-O bridged clusters that form NH2-MIL-101(Al).](image-url)
chemically resistant cartridges and temperature was controlled at the external wall of the PTFE inserts.

Time resolved SAXS–WAXS experiments were performed at the BM16 beamline of the European Synchrotron Radiation Facility, ESRF (Grenoble, France), and X9 beamline at the NSLS in Brookhaven (NY, USA). A bending magnet BM16b at ESRF was equipped with a Roper Scientific CCD camera PI SCX90-1300 mounted on a Newport RV240PE goniometer, and acquisition occurred with an X-ray research marCCD detector for WAXS and SAXS measurements, respectively. Indulator-based X9 at NSLS utilizes the marCCD SAXS detector and Photonic Science WAXS detector.

With the high-flux synchrotron radiation we were able to collect SAXS and WAXS patterns simultaneously with an excellent signal-to-noise ratio with a 20 s time resolution. The data were normalized for the intensity of the X-ray beam and corrected for detector sensitivity prior to background correction. The background scattering was subtracted.

3. Theory

3.1. SAXS analysis

The inverse Fourier transform of the intensity profile yields $\gamma(r)$, which is directly related to electron pair distance distribution function $p(r)$, a distinct characteristic for the morphology of a scattering entity (see SI). The $p(r)$ function is used to obtain information about the morphology of the scatterer as a function of time, during the growth process.

$$p(r) = \frac{r^2}{2\pi^2} \int_0^\infty q^2 dq \cdot I(q) \cdot \frac{\sin(qr)}{qr}$$  

(1)

To perform FT analysis, a smooth data spanning from 0 to $\infty$ is needed, but experimental SAXS data have a cut-off at the beam stop at small $q$-value, plus (often) a nonzero background value at large $q$, resulting in infinite values for the Fourier integral. The first problem can be solved by extrapolating SAXS data to $q=0$ by using an approximation derived by Guinier in 1939 for single particle scattering.

$$I_1(q) = \Delta n_{\text{exc}}^2 \exp\left[-\left(\frac{q R_g}{2}\right)^2\right]$$  

(2)

Here, $\Delta n_{\text{exc}}$ represents a contrast parameter, the excess of electrons of the scatterer relative to its surroundings, and $R_g$ is the radius of gyration, which is indicative for the size of the scatterer.

Further, the Porod volume $V$ is determined, an indicator for the volume of the scatterer:

$$V = \frac{2\pi^2 \cdot I_1(0)}{Q I}$$  

(3)

Finally, the scattering intensity is inversely proportional to the fourth power of $q$, as deduced by Porod in 1951 [64], which can be used to determine the specific free area of the scatterer, i.e. $S/V$.

$$S \quad V = \pi \times \lim_{q \to \infty} \frac{I(q)q^4}{Q}$$  

(4)

Detailed information on the equations and the role of ‘invariant’ $Q$ in Eqs. (3) and (4) is available in the supplementary information (SI).

The power law in Eq. (4) is used to extrapolate the $q$-space to infinity, using $I(q) = x_1 q^{-4} + x_2$. Here, $x_1$ represents $SOI/\pi V$ while $x_2$ corrects for incomplete subtraction of the background from experimental data. This data treatment yields a smooth dataset without Bragg peaks suitable for the application of Eqs. (2) and (4). The functions and parameters that can thus be calculated in this time-resolved experiment are: $p(r)$, $R_g$, $V$, and $S/V$. An example of this data treatment is given in Fig. 2.

When dealing with crystals that do not possess any high aspect ratios, deviation from the fourth power law of Porod might occur when the surface of the scatterer is not smooth. In that case $I(q)$ obeys behaviour of the form $q^a D_s(q)$ with $D_s$ representing the dimensionality of the surface fractal of the scatterer. Power law decay of the form $q^{-\alpha}$ with $\alpha = 4$ indicates a scatterer with a smooth surface. When $\alpha < 4$, one deals with rougher surfaces. As $\alpha$ approaches 3, one deals with surfaces of dominant fractal character. Fractal surface development is an important concept for MOFs, which are built up from smaller building blocks (e.g. trinuclear clusters) that have their influence on the full crystal scale.

3.2. Kinetic analysis

Analysis of the kinetic profiles was performed using the model developed by Gualtieri [65] and applied by Millange et al. [66] for the formation of several prototypical MOFs. This model is based on decoupling the nucleation and crystal growth processes. In such a way, the extent of crystallization (C) with time ($t$) can be simulated according to the following equation:

$$C = \left(1 + \exp\left(-\frac{1}{(t-a)/(b)}\right)\right) \left(1 - \exp\left(-(k_g t)^n\right)\right)$$  

(5)

Fitting a kinetic curve with this expression yields the parameterization of $a$, $b$ and $k_g$ (growth rate constant) and indirectly the nucleation rate constant, $k_n = 1/a$. In this work, as inferred from SAXS data evaluation, framework topology and the bi-pyramidal (MIL-101) and rhombohedral (MIL-53) shape of the final crystals and as suggested earlier by Millange et al. [48], it is assumed that MOF crystals grow in three dimensions ($n = 3$) and that nucleation is heterogeneous ($b = 15$).

4. Experimental results

Fig. 3 presents the time-resolved in situ WAXS and SAXS patterns recorded at 130 °C during the crystallization using high precursor concentrations in pure water (see Table 1). Under these conditions, only NH$_2$-MIL-53(Al) is formed, as inferred from the Bragg peak at $q = 6.2$ nm$^{-1}$ which corresponds to the (2 0 0) plane of NH$_2$-MIL-53(Al) in its narrow pore form [55]. First evidence of the MIL-53 phase formation can be observed at $\sim$700 s. The
SAXS decay, as shown in Fig. 3, follows power law behaviour $q^{-\alpha}$ with $\alpha$ increasing from 3.55 to 3.95 with time. These values are typical for growth of porous phases, as described for porous zeolites, indicating two processes, i.e. smoothening of the surface of the scattering particles and densification of the internal structure [67–69].

Porod volume development (Eq. (3)), is displayed in Fig. 4. The initial (first 200 s) drop represents dissolution of residual linker crystallites during temperature stabilization in the crystallization cell. Linker dissolution is followed by steady particle growth occurring in parallel with the development of the (2 0 0) reflection (Fig. 3). Crystallite morphology can be deduced from the calculated electron distance distribution function $p(r)$ (Fig. 5). The particle size growth is clearly reflected by the increasing intensity, while the maximum electron pair distance gives information about the shape of the particles. NH$_2$-MIL-53(Al) crystals possess an elongated character, in good agreement with the asymmetric curve shape of the $p(r)$ function (cf. Figs. 5 and 12 in [64,70]). The intensity grows in time as new crystals are created in a process of continuous nucleation. The maximum of the curve at $r=R_g$ corresponds with the radius of gyration. The highest value of $r$ corresponds to the maximum length of the scatterer, i.e. the particle size.

The increase in scatterer volume can be associated to nucleative crystal growth, in which the formation of the first primary units is the rate-limiting step [46]. Time-resolved plots for $R_g$ and $S/V$ are given in the SI, with trends similar to the Porod volume in Fig. 4. The constant shape of the $p(r)$ function with time (SI) is attributed to the fact that on average the particle morphology does not change, as expected for growth in three dimensions. It is emphasized however, that the average size of crystals observed during our experiments is always smaller than 90 nm because of the detection limits of the detector (the maximum detectable particle size follows $2\pi/q$).

Contrary to aqueous media, synthesis in pure DMF with low precursor concentrations (see Table 1) yields NH$_2$-MIL-101(Al) phase.

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Fig. 3. Time evolution of the WAXS pattern during the in situ synthesis of NH$_2$-MIL-53(Al) in H$_2$O @130 °C, with corresponding SAXS decays in log-log form (inset).

Fig. 4. Development of the Porod volume of scatterers during synthesis of NH$_2$-MIL-53(Al) in H$_2$O.

Fig. 5. $p(r)$ function during the synthesis of NH$_2$-MIL-53. The blue arrow indicates the increase of intensity and radius of gyration $R_g$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
The time evolutions of the WAXS pattern and SAXS decay, recorded at 130 °C, are shown in Fig. 6.

Before the MIL-101 crystalline planes, with dominant contributions by (1 1 1) and (1 1 3) planes [61], start to develop around 500 s, evidence for the early formation of the NH$_2$-MOF-235(Al) phase is clearly observed. MOF-235(Fe) was firstly described by Yaghi et al. [71] and identified as a precursor in the formation of MIL-53(Fe) by Walton et al. [66]. Later, we reported the formation of the isomorphous NH$_2$-MOF-235(Al) at early times during the formation of NH$_2$-MIL-101(Al) and NH$_2$-MIL-53(Al) in DMF and DMF/water mixtures [46].

Strikingly, SAXS decay does not vary in time exhibiting a constant slope with $\alpha = 3.8$. This value is indicative of scattering particles with a smooth surface. The Porod volume development (Fig. 7) initially displays some dissolution of the linker, but after that the volume of the scatterers remains constant, in agreement with calculated, invariant in time, values for $R_g$ and $S/V$ (see SI). The $p(r)$ function—also in strong contrast to MIL-53—shows constant intensity and shape. This implies that scattering entities with $\sim 25$ nm radius are formed rapidly before the measurements begin, with the diffraction peaks of NH$_2$-MOF-235(Al) and NH$_2$-MIL-101(Al) developing at about 500 s and 1500 s, respectively (Fig. 8).

Fig. 6. WAXS pattern with the formation of NH$_2$-MIL-101(Al) in DMF and corresponding SAXS decay (inset).

Fig. 7. Porod volume of scatterers during synthesis of amino MIL-101(Al) in DMF. No volumetric change is observed during growth of the crystalline phase.

Fig. 8. $p(r)$ function shows constant scatterer intensity and morphology during formation of NH$_2$-MIL-101(Al) in DMF, suggesting a slow solid-to-solid conversion.

Fig. 9 depicts the evolution in the WAXS and SAXS patterns for syntheses performed in DMF:H$_2$O = 9:1 mixtures at 130 °C at high precursor concentrations. The Bragg peak of NH$_2$-MOF-235(Al) is clearly visible right from the beginning of the synthesis (Fig. 9), and its fast appearance is ascribed to the higher precursor concentrations used (see SI).

Decay parameter values initially increase, but then decrease from $\alpha = 3.55$ to 3.00, pointing towards development of a surface with fractal (routher) character. The scattering intensities do however develop in time, pointing at an increasing number of scattering entities.

The evolution of the Porod volume (Fig. 10) provides perspective again. Dissolution of the linker is followed by rapid growth of volume of scattering entities (this is also seen for the Radius of Gyration, see SI), which in turn precedes gentler decline in volume. Comparing this with Fig. 9, the Bragg peak of NH$_2$-MOF-235(Al) really intensifies at the moment the Porod volume decay starts levelling off ($\sim 1500$ s) and gets more stable in time. Striking is the ‘step’ in intensity drop over the complete width of the $q$-length scale which accompanies this sudden crystallization; this is explained as an effect of the sudden formation of a porous crystalline structure from the non-crystalline scatterer. Further, the calculated $S/V$
values (SI) increase during the full period of time, this again points at a more complex, fractal nature of the surface, especially during the initial period.

The maximum of the $p(r)$ function (Fig. 11) increases while showing a shift to larger sizes, and then a shift to smaller sizes, pointing again at growth and shrinkage, without undergoing any significant morphologic change. The intensity, i.e. number of scattering entities keeps increasing during this process.

To complete the SAXS analysis, we fitted all kinetic profiles obtained from integration of the WAXS data using the above-mentioned Gualtieri equation. The fitting yielded nucleation and growth rate constants, $k_n$ and $k_g$, which are given in Tables 2 and 3. In case of NH$_2$–MIL-101(Al), from the Arrhenius plot activation energies for nucleation and growth were found to be $82 \pm 4$ and $94 \pm 6$ kJ/mol respectively, which is in the range of values reported previously for HKUST-1 and MOF-14 [48].

5. Discussion

The experimental results reported above demonstrate that important information can be extracted from SAXS profiles. It has to be considered that we deal with a poorly defined system, from the perspective of scattering entities, and therefore only part of the information obtained from the SAXS pattern is quantitative. That said, SAXS certainly adds value to our previous kinetic analysis [46] and allows chemical interpretation of the results, as discussed below.

We propose that NH$_2$–MIL-53(Al) forms through hydrolysis of AlCl$_3$·6H$_2$O. The formation of $\mu_2$-OH bridged Al polymorphs through hydrolysis of the hexaaqua aluminium complex in water

![Fig. 10. Time evolution of calculated Porod volume of scatterers during formation of NH$_2$-MOF-235(Al) in DMF:H$_2$O = 9:1.](image)

![Fig. 11. Time evolution of the $p(r)$ function during formation of NH$_2$-MOF-235(Al) in DMF:H$_2$O = 9:1.](image)

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Crystal growth and nucleation rate constants for NH$_2$–MIL-101(Al) crystallization extracted from the fitting of experimental profiles recorded at different temperatures. Syntheses were carried out in DMF under low precursors’ concentration (see Table 1).</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ (K)</td>
<td>$k_d$ ($\times 10^4$ s$^{-1}$)$^a$</td>
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<tr>
<td>---------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>393</td>
<td>2.3</td>
</tr>
<tr>
<td>403</td>
<td>6.3</td>
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<td>413</td>
<td>9.3</td>
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$^a$ All rate constants are determined with $\pm 10\%$ accuracy.

<table>
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<tr>
<th>Table 3</th>
<th>Crystal growth and nucleation rate constants for NH$_2$–MIL-53(Al) and NH$_2$–MIL-101(Al) crystallization in different solvent mixtures at 403 K.</th>
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<tbody>
<tr>
<td>Solvent composition (H$_2$O: DMF)$^a$</td>
<td>$k_d/10^4$ s$^{-1}$$^b$</td>
</tr>
<tr>
<td>NH$_2$–MIL-53(Al)</td>
<td></td>
</tr>
<tr>
<td>1:0</td>
<td>1.2</td>
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<tr>
<td>0.30:0.70</td>
<td>14.0</td>
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<tr>
<td>0.10:0.90</td>
<td>7.0</td>
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<tr>
<td>0.05:0.95</td>
<td>4.1</td>
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<tr>
<td>0:1$^c$</td>
<td>2.7</td>
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<tr>
<td>NH$_2$–MIL-101(Al)</td>
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<tr>
<td>0:1$^c$</td>
<td>13.0</td>
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</tbody>
</table>

$^a$ High concentration of the precursors.

$^b$ All rate constants are determined with $\pm 10\%$ accuracy.

$^c$ Note that two phases are formed simultaneously in these conditions.
has been thoroughly studied [72–75]. It has been claimed that equilibrium exists between the monomeric complex and the polymers it forms, favouring the former in non-basic solutions. This explains the relatively low yield and slow kinetics when pure water is used as solvent [46]. As expected for this mechanism, in which Al–O–Al chains steadily grow with 2-aminoterephthalic acid acting as crosslinker, one observes growth dominated by nucleation, densification of the porous phase and smoothening of the crystallite surface in SAXS. A similar nucleation control was earlier reported for ZIF-8 [45] and also observed during the electrochemical synthesis of NH2–MIL-53(Al) [63].

Whenever DMF is present, the intermediate phase NH2-MOF-253(Al) appears. This framework consists of μ3-O bridged, trigonal SBUs. This cluster is well known for d-block metals but was only recently also reported for p-block metals [76–78]. DMF seems to stabilize this cluster and an immediate result is a change in crystal growth and kinetics in comparison with the synthesis in water. It was already shown by Yaghi et al. that DMF acts as terminal ligand for Fe-based MOF-235 [71]. Moreover, it is well known that DMF can undergo decomposition at high temperatures, producing NM2H that would eventually provide a more basic medium, increasing in such case the crystallization kinetics, as observed in Table 3. The rationale behind solvent-induced stabilization of this phase is at this point unknown, and is currently investigated by our group. In SAXS, we observe unusually fast growth of scattering particles of an amorphous phase. But as these then slowly shrink, this phase changes into crystalline NH2-MOF-235. We propose that the amorphous phase consists of π-stacked SBUs which arrange into NH2-MIL-253(Al) as AlCl4- anions diffuse into the voids, balance charge of the cluster and create the crystalline phase. During this process the fractal character of the crystals and their roughness increase, as indicated by the change in slope in the SAXS decay (Fig. 10). NH2-MOF-235(Al) is then only slowly transformed into NH2-MIL-53(Al) over a long period of time (+48 h) [46]. In any case, yield improves tremendously after an extended period of synthesis. It appears that the equilibrium between MOF-235 and MIL-53 structure is favourable towards the latter.

Pure DMF has to be used to obtain NH2-MIL-101(Al). From chemical perspective, only removing the terminal aqua ligand is necessary to convert NH2-MOF-235(Al) into NH2-MIL-101(Al) (see Fig. 12), which might be the reason behind the constant scatterer volume, morphology and surface in time. This could be rationalized by a crystal rearrangement, rather than a formation–dissolution–formation mechanism, as proposed earlier [46]. Previous work by Bras et al. drew similar conclusions from analogous analysis for the formation of aluminophosphates crystallizing from thick gels, were diffusion would be limited [79]. The synthesis in anhydrous DMF is unique as it is the only reported route towards NH2-MIL-101(Al). It seems that only in pure DMF, reaction of the aqua ligand and aluminium tetrachloride anion to form a hydroxyl ligand and hydrochloric acid is favourable. Enhanced stability of hydrochloric acid in DMF solvent has been demonstrated in literature before [80].

6. Conclusions

In this work, we have used synchrotron-based SAXS technique backed by WAXS, for the in situ study of MOF growth. It was possible to monitor the temporal development of size, morphology, and crystallinity of two of the important MOF topologies, MIL-53 and MIL-101. Based on the information obtained, description of the formation of these frameworks nears completion. Although the macroscopic developments on full crystal scale are now documented for different solvent systems, the chemistry behind MOF-235 and its transformation into MIL-53 and/or MIL-101 should be further studied using complementary in situ techniques, i.e. EXAFS and NMR.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2012.08.044.

References
