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Subtle polymorphism of zinc imidazolate frameworks: temperature-dependent ground states in the energy landscape revealed by experiment and theory†

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We show by variable-temperature X-ray diffraction and differential scanning calorimetry experiments that zinc imidazolates with coi and zni framework topology, respectively represent the thermodynamically stable phase below and above a transition temperature of ≈360 °C at ambient pressure. The relative stability of the two polymorphs and the experimentally observed strong negative thermal expansion of the coi phase at high temperatures close to the phase transition were successfully modelled using density functional theory calculations. A novel metastable zinc imidazolate with neb framework topology was detected in situ X-ray diffraction experiments as a transient crystalline phase during solvothermal crystallisation of the stable coi phase.

Zeolitic imidazolate frameworks (ZIFs) represent a new class of technology relevant microporous materials that are at the focus of current research efforts.1,2 Important characteristics of ZIFs are comparatively high thermal and chemical stabilities and the ability to crystallise in a large variety of topologically different frameworks which may be tailored for a specific application in gas storage, separation, sensing or catalysis. ZIFs consist of tetrahedral cationic centres (ZnII, CoII, FeII, CdII, and also LiI or NaI) connected by imidazolate-based bridging ligands. Because of the local tetrahedral geometry of metal connectors and the metal–imidazolate–metal bridging angle of ≈145° ZIFs adopt network topologies common for microporous silica polymorphs and zeolites. Recent studies have revealed that ZIFs may undergo thermally- and/or pressure-induced amorphisation that reinforces the similarity between ZIFs and silica.3–5 However, important differences between ZIFs and silica systems are still ignored in the literature. For example, it is well known that the thermodynamic ‘ground state’ of the silica system at ambient conditions corresponds to the α-quartz phase (qtz net)6, whereas the quartz-like topology is hardly accessible in the Zn(im)2 (im = imidazolate) system as was shown in our previous ab initio study.7 By considering only unsubstituted imidazolate bridging ligands, nine topologically different Zn(im)2 frameworks have been experimentally realised to date (zni, coi, cag, mer, gis, df, crb, zec, ngs)1,2,9 and even more are predicted to be synthetically accessible.7

However, up to now there was no experimental study which addressed the important question about the thermodynamically most stable phase(s) (‘ground state(s)’) in the Zn(im)2 system, which might be either of the two most dense phases zni or coi. Recently, an irreversible single-crystal-to-single-crystal pressure-induced phase transition from the zni to the coi phase was observed at room temperature by Spencer et al.10 revealing that coi is stable at high pressures (≥0.55 GPa). The polymorphs with zni and coi underlying nets crystallise in the tetragonal space groups I41cd and I41, respectively, and are closely related to each other since both frameworks may be considered as being built up from triple helices connected in different ways (Fig. 1). By now, the coi phase was disregarded in theoretical calculations and the zni phase was assumed to be the most stable phase.7,8,11,12 In this Communication, we address the question of the ‘ground state’ in the Zn(im)2 system from both an experimental and computational point of view.

Variable-temperature X-ray diffraction (XRD) patterns taken from coi powder samples at ambient pressure reveal that a phase transition to zni takes place at ≈360 °C (Fig. 2a). The zni phase decomposes in air at ≈410 °C. On differential scanning calorimetry (DSC) curves measured during heating of coi powder an endothermic peak is seen at 349.0 °C (Fig. 2b) in reasonable agreement with the XRD data when considering the different heating rates. The endothermic transition enthalpy proves that the coi phase is the thermodynamically stable phase below the transition temperature, i.e. the coi phase represents the low-temperature and the zni phase represents the high-temperature

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phase at ambient pressure. This is in line with the reported room-
temperature densities ($\rho_{\text{coi}} > \rho_{\text{zni}}$). The phase transition is
irreversible and the resultant zni phase can be recovered at room
temperature. The experimental transition enthalpy of the
coi–zni transition determined by DSC amounts to
$\Delta H_{\text{exp}} = 2.9 (1) \text{ kJ mol}^{-1}$
being in fair agreement with the value obtained by density
functional theory (DFT) calculations [$\Delta H_{\text{PBE}} = 5.8 \text{ kJ mol}^{-1}$].
Commonly used generalized gradient approximation (GGA)
functional (PBE) allowed for good geometry descriptions of the
coi and zni structures (see ESIef{footnote}) and yielded an energy difference
of $\Delta E_{\text{zni–coi}} = 0.06 \text{ eV/[Zn(im)]}_2$ (at 0 K). However, to achieve a
quantitative agreement with experimental values, the enthalpy
difference was estimated with the recently developed non-local van
der Waals DFT functional (see ESIef{footnote}) being capable of describing
dispersion forces, which are important to properly account for
inter-ligand interactions. The enthalpy difference in this case
amounts to $\Delta H_{\text{v10}} = 1.6 \text{ kJ mol}^{-1}$, and is in good agreement with
the experimental value.

The reflections in the variable-temperature XRD patterns (Fig. 2a) show that the coi phase undergoes structural changes with changes in temperature. The variation of the unit cell parameters as a function of temperature is presented in Fig. 3a. Up to $\approx 280 \text{ °C}$ the cell volume slightly increases with temperature. This results from an increase of the tetragonal $a$ (and $b$) axis while the $c$ axis is constantly decreasing. Strikingly, above $\approx 280 \text{ °C}$ up to the phase transition at $\approx 360 \text{ °C}$ the cell volume strongly shrinks due to contraction of the $c$ as well as the $a$ axes. At the coi–zni transition the cell axes change by $\Delta a = +0.490 \text{ Å (2.15%)}$ and $\Delta c = -0.654 \text{ Å (−5.12%)}$ resulting in a small contraction of the cell volume by $\Delta V = -67 \text{ Å}^3 (−1.0\%)$, i.e. zni becomes the most dense phase above $\approx 360 \text{ °C}$.

Note that negative thermal expansion (NTE) is more commonly
found/predicted for microporous zeolites and metal–organic
frameworks (MOFs). For example, the cubic MOF HKUST-1
shows as an isotropic linear coefficient of the thermal expansion
of $a_L = dL/(LdT) = 2.41 \times 10^{-6} \text{ K}^{-1}$. In contrast, in the
temperature range 310–350 °C coi has near-linear thermal
expansion coefficients parallel to the $a$ and $c$ axis of $a_a = 2.112$
$\times 10^{-6} \text{ K}^{-1}$ and $a_c = 2.188 \times 10^{-6} \text{ K}^{-1}$, respectively (Fig. 3b). The
values are nearly two orders of magnitude more negative than that
for HKUST-1 and close to the maximum NTE behaviour reported
so far for framework materials.

This interesting thermal behaviour was investigated with
constant temperature, constant pressure ab initio molecular
dynamics (MD) simulations. MD runs were performed at different
temperatures in the experimentally relevant range 227–377 °C.
Based on a 272 atom primitive cell the cell volume was found to
expand as a function of temperature in the lower temperature
range in agreement with experiment. The calculations at 347 °C show a
tendency towards lengthening (some of) the Zn–N
coordination bonds and the formation of trigonal–pyramidal centres (Fig. 4a) and at 377 °C the formation of ‘trigonal’ coordination environments (Fig. 4b). In the latter geometry one ligand has left and another ligand has not yet entered the coordination sphere. Both the \( a \) and \( c \) axes shrink in response to this. This effect is coupled with changes (typically, shortenings) in H–H distances, which are the most relevant non-bonding interactions in the system, as evidenced by monitoring their evolution during MD runs (see ESI†). On forming ‘trigonal’ centres the axis shortening ratio amounts to \( \Delta a/\Delta c = 1.06 \) (see ESI†) which is in very good agreement with the corresponding ratio of the experimental data of \( \Delta a/\Delta c = (a_{350} - a_{310})/(c_{350} - c_{310}) = 1.1 \) (Fig. 3b). Rather than a partial amorphisation process the appearance of ‘trigonal’ centres is an intermediate stage of the transition into the Zn–N contact at 5.9 Å. In the activated stage (377 °C) two ‘non-bonding’ Zn–N contacts fall below 3.8 Å, which allows for ligand reshuffling. The longer ‘non-bonding’ distances (≥6 Å) at lower temperatures make Zn tetrahedron inversion unlikely.

The mechanistic insight into the phase transition obtained from theory is also of interest with regard to the recently reported thermally-induced amorphisation of various microporous Zn(im)_2 phases (cag, dft, bct) at temperatures of 280–300 °C and the
recrystallisation of amorphous Zn(im)_2 to zni at ≈ 360 °C. Strikingly, the former and latter temperatures exactly correspond to the beginning of volume contraction of the coi phase and the point of crossover of stability of the coi and zni phases, respectively. Thus, the experimentally observed amorphisation of the cag, dft, and bct phases might have become possible due to a high activation barrier for the nucleation of the stable crystalline coi phase below ≈ 360 °C.

Indeed, our experience with synthesising the coi phase from solution shows that its nucleation is a rather unfavourable process while the zni phase is readily obtained by precipitation from solution – as a metastable phase – under a wide range of conditions in line with Ostwald’s rule of stages. Once the zni phase has formed it does apparently not transform into the stable coi phase when kept under the mother solution, probably due to low differences in solubility as a result of nearly equal total energies (see above). Only very few wet-chemical synthetic protocols for coi have been reported. We synthesised the coi phase according to a recent report under solvothermal conditions from ethanol–pyridine mixture solutions which are rather specific conditions. Thereby, we discovered for the first time that coi formation involves the transient crystallisation of a novel phase. According to powder and single-crystal XRD and TG studies this novel metastable phase possesses the composition [Zn(im)2]0.5py and neb framework topology (see ESI†). Only a Co analogue had been reported before. The neb phase forms at room temperature within a period of about 10 to 120 minutes depending on the composition of the reaction mixture. Upon solvothermal treatment at about 140 °C the intermediate neb phase converts with release of pyridine into the stable coi phase (see ESI†). This was monitored in situ by time-resolved energy-dispersive X-ray diffraction (EDXRD) experiments.

As can be seen from the EDXRD spectra and corresponding extent of reaction data (Fig. 5) the conversion takes place rather sharply and involves the dissolution of a significant fraction (~ 0.5) of the intermediate neb phase before coi starts crystallising, suggesting that the conversion is not a solid–solid transformation but rather a solution–mediated recrystallisation process as might be expected from the different framework topologies and chemical compositions. While crystalline intermediates during ZIF formation have been reported previously, this is the first direct in situ monitoring of a ZIF conversion process in solution. We speculate that nucleation of the coi phase takes place heterogeneously on the surfaces of still available neb particles. This was indicated by the observation that pure-phase coi was only obtained if the neb-containing suspension was vigorously stirred (as during the EDXRD experiments). Solvothermal treatment of unstirred solutions yielded under otherwise similar conditions mixtures of coi and zni (see ESI†). This suggests that stirring leads to close contact between the surfaces of the neb particles and the solution and thereby favours the nucleation of the coi phase. An alternative explanation might be that due to stirring, the overall level of supersaturation is kept low allowing homogeneous nucleation of the stable (less soluble) coi phase while simultaneously excluding nucleation of the metastable (more soluble) zni phase because higher levels of local supersaturation are avoided. Either reasoning could explain the difficulties of preparing the stable coi phase. It is also difficult to prepare the coi phase via thermal treatment of the novel neb phase in the solid state. TG and variable-temperature XRD studies (see ESI† Fig. S7 and S8) revealed that during escape of pyridine molecules the neb framework structure collapses yielding, besides coi, an amorphous material and zni.

In conclusion, our joint experimental and computational studies have clarified that in the Zn(im)_2 system the coi and zni phases, respectively, represent the thermodynamically stable phase below and above a transition temperature of ≈ 360 °C at ambient pressure. Therefore, it is reasonable to assume that above
the transition temperature the pressure-induced \( \text{Zn}^{(im)}_2 \) phase transition should not take place, i.e. the role of the pressure would be mimicked by increased temperature and the accompanying volume reduction. The experimentally observed strong NTE of the \( \text{coi} \) phase at high temperatures close to the phase transition was successfully modelled by DFT calculations and related to the role of inter-ligand interactions which are mainly affected by the volume reduction and finally induce the phase transition by forming ‘trigonal’ \( \text{Zn} \) centres, a reactive step towards the transition to the \( \text{Zn} \) phase. A novel metastable \( \text{neb} \) phase was detected as a transient phase during solvothermal crystallisation of the stable \( \text{coi} \) phase. The results presented here significantly advance our understanding of the \( \text{Zn}(\text{im})_2 \) and possibly other ZIF systems with regard to phase stabilities, phase transitions and phase formation (synthesis).

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