Cage Compounds

Engineering Porous Organic Cage Crystals with Increased Acid Gas Resistance


Abstract: Both known and new CC3-based porous organic cages are prepared and exposed to acidic SO2 in vapor and liquid conditions. Distinct differences in the stability of the CC3 cages exist depending on the chirality of the diamine linkers used. The acid catalyzed CC3 degradation mechanism is probed via in situ IR and a degradation pathway is proposed and supported with computational results. CC3 crystals synthesized with racemic mixtures of diaminocyclohexane exhibited enhanced stability compared to CC3-R and CC3-S. Confocal fluorescent microscope images reveal that the stability difference in CC3 species originates from an abundance of mesoporous grain boundaries in CC3-R and CC3-S, allowing facile access of aqueous SO2 throughout the crystal, promoting decomposition. These grain boundaries are absent from CC3 crystals made with racemic linkers.

Traditional nanoporous materials such as zeolites and more recently metal–organic frameworks (MOFs) have been studied extensively for use in catalysis and molecular separation processes because of their shape selectivity, large pore volume, and uniform pore dimensions.[1] These materials are extended crystalline frameworks in two or three dimensions with repeating porosity over the length scale of the entire crystal. However, porous organic cages (POCs) are individual molecules with an intrinsic cavity; that is, they are nanoporous molecules.[2] They can be dissolved in common organic solvents without altering the porosity of an individual cage and can be packed into solid form upon solvent removal to give a three-dimensional pore network. This connected pore network results from intrinsic cavities connected by openings between adjacent porous molecules.[3,4] POCs have many appealing properties relative to crystalline framework nanoporous materials such as ease of modification, mobility, and importantly, solution processability, as highlighted in a recent review from Cooper and co-workers.[5]

Primarily owing to the allure of solution processable nanoporous crystals and the interesting applications such a feature enables, POCs have been studied for gas separation, adsorption, molecular recognition, and sensing.[6] More recently, the concept of porous liquids (PLs) utilizing POCs was experimentally discovered. These are liquids that have permanent, well-defined cavities. This idea was first put forward in a theoretical paper[7] and was recently demonstrated experimentally with several imine-based POCs.[8]

The concept of porous liquids combines the permanent pores found in conventional porous materials with liquid-like properties, which introduces the possibility of enhancing existing liquid-based chemical processes such as scrubbing and liquid–liquid extraction. Two issues that any new material must certainly face in these applications are 1) the stability of the material in the face of aggressive contaminants such as H2S, SO2, NOx, and water,[9] and 2) the scalability of the production of the material. Here, the stability of imine-based cages was investigated using CC3 as a model compound for studying SO2 contamination, as SO2 is usually present in significant concentrations in industrial gases such as flue gas from coal-fired power stations. The chemical and physical degradation mechanism of CC3-R exposed to dilute SO2 conditions is thus developed. We also describe a reduced-cost method for the synthesis of CC3-like molecules. This method is shown to enhance acid stability relative to the chiral CC3-R or CC3-S. This increased stability is attributed to a decrease in mesoporous planar defects in POC crystals, an effect visualized by confocal fluorescent microscopy.

CC3-R was synthesized according to literature[3] The diffraction patterns of the crystals matched the calculated powder pattern and the BET surface area was estimated to be 427 m² g⁻¹ from N2 physisorption (Figure 1). To assess the interaction between CC3-R and SO2, the sample was loaded in an in situ DRIFT-IR cell and exposed to dilute SO2 gas (the experimental setup described in the Supporting Information, Section S2).

The differential spectra (that is, the SO2-exposed spectra relative to the neat CC3-R spectra) at different times during the exposure (Figure 2b) reveal chemical bond evolution during the interaction with the humid acid gas. Positive peaks indicate

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occurrence of new species, and negative peaks indicate diminishing species. A potential chemical degradation mechanism was developed utilizing these in situ IR experiments and both the vibrational modes and corresponding IR frequencies of various species that are formed during degradation were calculated using DFT methods. First, the imine bond in pristine CC3-R is attacked by HSO$_3^-$ and H$^+$, forming a decomposition intermediate shown in Figure 2c. This intermediate structure becomes a broken cage with a dangling amine group and aldehyde group as shown in Figure 2d. Finally, SO$_2$ can easily interact with the newly generated amine groups to form –NH$_2$–SO$_2$ complexes (Supporting Information, Figure S3c). The imine hydrolysis pathway was not explicitly considered here as the cages have been found to be stable in boiling water for at least 4 h.$^{[10]}$ Major peaks assigned from DFT calculations are labeled in Figure 2b. A complete peak assignment can be found in the Supporting Information, Table S1. In general, good agreement between the calculated and experimental results was observed, although some minor deviations are still present.

The samples recovered from the in situ IR experiments exhibited minimal deviations in crystallinity and morphology relative to the pristine samples. In an effort to further understand the chemical and physical degradation mechanisms of CC3 crystals, extended exposure times in humid vapor and aqueous acid conditions were investigated.

The SO$_2$ stability of both CC3-R and CC3-S were first investigated under humid vapor conditions. Samples were exposed to 50 ppm SO$_2$ for two and four days at 80% relative humidity at room temperature.$^{[11]}$ The morphology of the samples exposed to these conditions was examined by SEM (Figure 3; Supporting Information, Figure S5). After the two-day exposure, the octahedral shapes of both CC3-R and CC3-S were maintained; however, irregular thin cracks were formed inside the crystal (Supporting Information, Figure S5 1a,b). A higher number density of acid-induced cracks was observed at longer exposure times (Figure 3a; Supporting Information, Figure S5 2a,b). The crystallinity of both two-day and four-day exposed samples were estimated using PXRD, and no loss in crystallinity was observed (Supporting Information, Figure S6). FTIR spectra were taken after the acid gas exposure as well as after the samples were washed with ethanol. For the samples

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**Figure 1.** a) Synthetic route of CC3-R from 1,3,5-triformylbenzene and ((R,R)-1,2-diaminocyclohexane; b) SEM image of octahedral CC3-R crystals; c) Rietveld refinement of powder X-ray diffraction pattern of CC3-R; and d) N$_2$ adsorption–desorption of CC3-R at 77 K.

**Figure 2.** a) Proposed degradation pathway–imine bond cleavage facilitated by HSO$_3^-$; b) IR spectra obtained during different time intervals of SO$_2$ adsorption on CC3-R; major peaks are labeled with the corresponding color of the structures in (a); c) relaxed structure of decomposition intermediate of CC3-R; and d) relaxed structure of the broken cage and –NH$_2$–SO$_2$ complex.

**Figure 3.** Morphological changes of a) CC3-S and b) CC3-mix after humid SO$_2$ exposure for four days; c) CC3-S and d) CC3-mix after aqueous-phase SO$_2$ exposure (1000 ppm equivalent).
exposed to acid gas for two days, no apparent difference in the spectra were found (Supporting Information, Figure S7). However, for the samples exposed for four days, new absorption peaks corresponding to C=O and N–H bonds were observed (Supporting Information, Figure S8), in excellent agreement with the in situ IR experiments. Those signature vibrations diminished after the samples were washed with ethanol, indicating that free linkers formed during cage decomposition were mobile.

A comparison of the water sorption isotherms (Supporting Information, Figure S13) and the pore volume of CC3 derived from N2 physisorption indicates that relative humidity greater than 80% resulted in pore filling with liquid-like water within the pores of CC3. This “liquid-like” adsorbed water creates a similar chemical environment in high humidity and aqueous experiments. The SO2 stability of the materials was then studied in aqueous conditions as an extension to the humid SO2 vapor exposure experiments. The liquid-phase SO2 concentrations correspond to approximately A) 20 ppm, B) 1000 ppm, and C) 10000 ppm of gas-phase concentrations. CC3-R soaked in a 20 ppm equivalent solution was eroded on the surface and small holes and cracks were visible under SEM (Supporting Information, Figure S5 3a). At a higher acid concentration (1000 ppm), all the CC3-R crystals exhibited broadened cracks compared to the humid exposure result (Supporting Information, Figure S5 4a). These cracks were also observed using fluorescent confocal microscopy (Supporting Information, Figure S9). Images at different depths of the crystal showed interlinked cracks throughout the crystal, which likely originated from grain boundaries in the CC3-R and CC3-S crystals (the effect of these grain boundaries will be discussed in detail later in the article). The 10000 ppm equivalent solution dissolved the cages. CC3-S exhibited identical morphological changes to CC3-R under all acid concentrations (Figure 3 c), as expected.

CC3-R was washed with ethanol after aqueous SO2 exposure and showed C=O and N–H bond vibrations in the FTIR spectrum (Supporting Information, Figure S10). The broken or damaged cages on the surface were likely washed off during the collection of the crystals from the SO2 solution. Therefore, the C=O and N–H vibrations observable in the FTIR spectra should originate from damaged cages inside the crystal that cannot diffuse out through the pores of the CC3 crystals and were thus left inside. The crystallinity of aqueous SO2 treated CC3-R and CC3-mix was examined by PXRD (Supporting Information, Figure S11). For CC3-R, the reflection at 6.1° 2θ ([111] crystal face) becomes more pronounced while the relative intensity of other reflections remains unchanged. The most significant change is that the reflections at 15.42° 2θ and 15.82° 2θ disappeared. These two reflections correspond to the [331] and [420] crystal faces, respectively. Their disappearance is consistent with imine bond cleavage, which was also suggested by FTIR measurements.

As noted by Cooper and co-workers, CC3-R and CC3-S cages can efficiently pack together by chiral recognition and instantaneously precipitate from the mixing of CC3-R and CC3-S solutions (crystals resulting from precipitation are denoted as CC3-ARS herein[10]. This observation was explained by the high packing energy between cages containing (R,R)- and (S,S)-1,2-diaminocyclohexane. Although the shape and size of the CC3-RS crystals can be controlled by varying the temperature and mixing rate, the resulting crystals tend to be quite small (< 500 nm).

Here, we attempt to enhance the stability of CC3-R crystals by using a low-cost racemic mixture of diaminocyclohexane during the synthesis of CC3. Instead of mixing pre-formed CC3-R and CC3-S cages, mixed linker CC3 cages were synthesized as shown in Figure 4a. This molecule has two stereocen-

![Figure 4](image)

**Figure 4.** a) Synthesis routes of various CC3 species and characterization of CC3 species: b) Powder diffraction patterns, c) 13C SS-NMR, d) N2 physisorption isotherm at 77 K, and e) CO2 physisorption isotherm at 308 K of CC3-R, CC3-S, CC3-tran, and CC3-mix.
tions for CC3-trans and CC3-mix shift to higher 2θ positions relative to CC3-R. Rietveld refinement indicated that CC3-mix cage molecules pack more densely than CC3-R (Supporting Information, Figure S15). Despite this tighter packing, CC3-trans and CC3-mix showed higher N₂ and CO₂ uptake relative to CC3-R/CC3-S (Figure 4d,e).

Although synthesized under the same conditions, CC3-trans and CC3-mix crystals have smaller sizes and smoother crystal surfaces than CC3-R and CC3-S crystals. The difference in the sizes of the crystals likely originates from the faster nucleation rate in the CC3 crystals grown using a mixture of diamine isomers. Racemic cage pair interactions have been noted to be more favorable than homochiral cage pair interactions.[3, 12] In the CC3-trans and CC3-mix cases, although each cage contains different chiral linkers, the packing is still more favorable than for enantiopure cages. The lack of strong interactions in CC3-R and CC3-S molecular packing results in more mesoscale defects such as grain boundaries in the crystal, which were visualized by fluorescent confocal microscopy (Figure 5).

Fluorescein sodium salt was impregnated into the crystal as a dye molecule that is large enough to be excluded from the nanopores in CC3 but can access the space between crystal grains. The images taken at different depths in the CC3 crystals clearly highlight in CC3-R and CC3-S, whereas no grain boundaries are observable in the CC3-trans and CC3-mix samples.

In contrast to the observations of CC3-R and CC3-S, CC3-trans and CC3-mix exhibited only minor surface layer exfoliation (Figure 3b,d; Supporting Information, Figure S5 column 3,4) in both humid and aqueous SO₂ exposure conditions. Although CC3-mix exhibits some surface morphology changes, the bulk chemical structure has not changed. These observations are consistent with a shrinking core corrosion model, which would be expected with a lack of mesoscale grain boundaries that would permit aqueous acid and liquid-like adsorbed water/acid mixtures to have access throughout the CC3 crystal (Scheme 1).

The gas sorption properties of the acid-treated samples were compared with the neat materials and summarized in the Supporting Information, Figure S12. The BET surface areas of CC3-R and CC3-S decreased with increasing acid exposure time/concentration. The CO₂ uptake of CC3-R and CC3-S increased after acid gas exposure. This is attributed to the favorable interactions of CO₂ with amines in partially damaged cages in the crystal. For CC3-mix, the surface area and CO₂ uptake were generally unaltered. However, over 50% loss in surface area and CO₂ uptake was observed after four-day humid exposure for CC3-trans. The different behavior between CC3-trans and CC3-mix was attributed to integration of cis-di-aminocyclohexane in the CC3-mix cage. The cis isomer content was determined to be approximately 30% according to ¹H NMR (Supporting Information, Figure S16); however, attempts to synthesize CC3 using pure cis isomers yields a glassy polymer. The exact mechanism of the stability conferred by the cis stereoisomer is currently not understood.

The decomposition of CC3 species in the presence of SO₂ and H₂O vapor or liquid happens at the molecular level (that is, individual cages). The imine bond connecting the two linkers within an individual cage dissociates when challenged with high concentrations of humid acid gas or aqueous acid solutions. Although the total water uptake of CC3-trans and CC3-mix is comparable, the minor difference in the extent of surface erosion is also related to the significant difference in water adsorption at the same relative humidity. Indeed, “liquid-like” water does not occur in CC3-mix and CC3-trans until high
relative humidities (Supporting Information, Figure S13; 85% RH). The combination of elimination of grain boundaries as well as decrease in water uptake both contribute to the increase in chemical resistance of CC3-mix relative to CC3-R or CC3-S.

In summary, the degradation of imine-bond based porous organic cages under SO2 conditions was studied with in situ IR experiments and DFT calculations. The synthesis of CC3 variants with mixed linkers at the molecular level is reported. The linkers with different chirality increased the stability of the resulting cages packed into the solid state. This is shown from decreased solubility in common solvents and increased SO2 stability, as observed through electron microscopy, textural, spectral, and crystallographic analysis. Samples of CC3-R and CC3-S in both humid vapor and aqueous SO2 exposure conditions showed severe decomposition while CC3-mix and CC3-trans showed only mild surface changes and no bulk property changes. The morphological differences in the two sample types and their acid-induced degradation was probed by fluorescent confocal microscopy; mesoporous grain boundaries in CC3-R and CC3-S (but not CC3-mix and CC3-trans) were observed. These mesoporous grain boundaries in CC3-R and CC3-S accelerated the corrosion due to reaction with SO2 and water, as the acid can access surfaces small crystal grains throughout the CC3-R crystals. The good stability and preserved CO2 uptake reveals CC3-mix as a potential candidate for enhancing membrane separations in aggressive industrial conditions. We also note that the self-synthesized 1,3,5-benzencarbaldehyde and racemic diaminocyclohexane used in CC3-trans and CC3-mix reduced the cost to one tenth of the original expected cost, which makes this material more cost-effective for use in large scale applications.

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