High Pressure synthesis of *all-transoid* polycarbonyl [-(C=O)-]$_n$ in a zeolite.

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Supporting Information

ABSTRACT: Polymeric carbon monoxide (pCO) was synthesized in the micropores of silicalite, a hydrophobic, all SiO_2 zeolite at 7.0-7.5 GPa in a diamond anvil cell. Vibrational spectroscopy and single crystal X-ray diffraction data on samples at ambient pressure show that the embedded pCO in silicalite is compatible with the ideal [-(C=O)-]$_n$ polycarbonyl chain, which has been predicted, but never been obtained so far. The unique pCO chain/silicalite material is a nano-composite crystal with four guest pCO chains per host unit cell, which may exhibit high energy storage capability. This study demonstrates the capability of strong confinement in driving the ordered self-assembly of dense molecular systems in a well tailored fashion.

High pressure polymerization of simple molecules (C_2H_2, C_2H_4, C_6H_6, CO_2, N_2 ...) is a hot topic in chemistry, condensed matter physics, and materials science[1,2,3,4,5,6,7,8,9]. The case of CO is particularly intriguing as this is a very simple molecule with a weak static dipole moment, which is isoelectronic, but much more reactive than N_2. Indeed, the formation of polymeric CO, pCO, in the GPa pressure range has been investigated in a number of experimental and computational studies[10,11,12,13,14,15,16,17,18]. This material is an amorphous solid including carbonyl groups with structural and orientational disorder and can even be non stoichiometric and may disproportionate with the formation of CO_2. This polymer is highly photosensitive, hygroscopic and metastable at ambient conditions, where it has been shown to be capable of storing energy of several kJ/g[14]. Based on a recent study by FTIR spectroscopy, it was shown that high pressure pCO is a random 3D polymer made of a large variety of functional groups such as C=O carbonyls, particularly in the form anhydride moieties, epoxy rings, C-C-O and C-O-C groups with also an excess of molecular CO_2; once exposed to the atmosphere, the reaction product readily and irreversibly reacts with water giving rise to carboxylic groups[19].

A recent DFT study[20] predicted that orientationally and structurally ordered pCO can be obtained at high pressures in the form of a crystalline, metallic phase made of 1D, [-(C=O)-]$_n$ chains with alternate head-to-tail orientation of C=O (fig. 1), or either layered or 3D insulating CO crystal structures where carbon atoms are all in sp^3 hybridization.

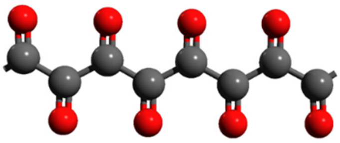

Figure 1. [-(C=O)-]$_n$ polycarbonyl chain with alternate head-to-tail orientation of C=O. Grey (red) balls: C (O) atoms.

Although these extended phases are expected to be much more stable above several GPa than all molecular CO crystals by even 1 eV/CO molecule, their energy relationship with respect to the disordered pCO solids obtained so far is not known. It is thus not possible to understand why these crystalline phases were never obtained experimentally, i.e. whether their potential formation is thermodynamically or kinetically hindered. In fact, one possible reason of kinetic hindering is the head-to-tail disorder of the CO molecules in all molecular, condensed phases from where the polymerization is initiated. Remarkably, the 1D chain phase of ordered pCO is expected to be definitely more stable than all molecular CO solid phases at ambient pressure, and to be highly metastable/energetic with respect to decomposition into C and CO_2 with a stored energy of about 1 eV/molecule (~3.5 kJ/g)[20].

In this work, we demonstrate the feasibility of inducing the self-assembly of dense CO in the spatially sub-nanoconfined region of the channels of an electrically neutral, non-catalytic, hydrophobic, all SiO_2 zeolite, silicalite. Silicalite is characterized by a framework of 4-, 5-, 6- and 10-membered rings of corner-sharing SiO_4 tetrahedra forming interconnected, mutually orthogonal straight and sinusoidal 5.5Å diameter channels (ref. 21 and 22 and references therein). The insertion of simple guest molecules such as Ar and CO_2 in the channels of this zeolite deactivates the pressure induced amorphization of the framework up to at least 25 GPa[23,24,25,26,27]. We have recently observed that this kind of confinement can drive the high pressure polymerization of simple, unsaturated molecules such as C_2H_2 and C_2H_4 in such a way as to obtain polymeric chains with a structure and possibly physical properties different from those observed in the bulk polymers[28,29]. The ensemble of these embedded, guest polymers and the host zeolite framework constitutes what should be considered as an entirely novel class of organic/inorganic hybrid materials, potentially exhibiting physical properties of technological interest. In the following, we show that the purely high pressure polymerization of CO in silicalite, leads to the formation of a unique pCO/silicalite composite material (pCOSIL) with a structure compatible with the ideal, structurally and orientationally ordered $[-(C{=}O)-]_n$ chains predicted by DFT calculations.

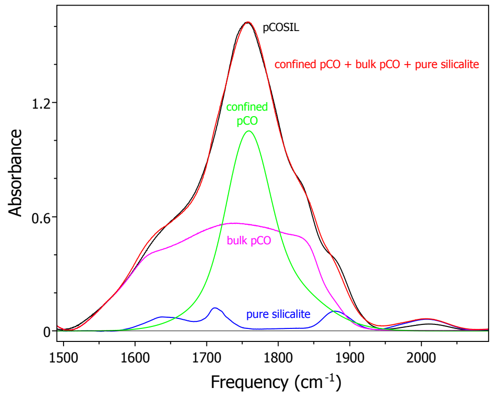

Figure 2. IR absorption spectra, in the C=O stretching region of recovered samples in the gasket, taken out the DACs and exposed to atmosphere. Black: pCOSIL. Magenta: (rescaled) pure, bulk pCO. Blue: (rescaled) pure silicalite. Green: analytical peak for confined pCO in the silicalite. Red: sum of the rescaled spectra of bulk pCO, silicalite and confined pCO fitting the spectrum of pCOSIL.

Diamond anvil cells (DAC) were used for the high-pressure synthesis of pCOSIL, starting from mixtures of CO and powder or single crystal (size: 80×40×40 µm³) hydrophobic silicalite 1-F. Description of the material characterization set-ups: IR, Raman and single crystal X-ray diffraction, and of *ab initio* computational methods for calculating the vibrational spectrum of pCO are reported in SI.

The conversion of CO to pCO at 7.0-7.5 GPa had typical time constants of 1 h or less and reached almost 90% after several days, as monitored by IR spectroscopy. In the recovered samples at ambient pressure, bulk pCO strongly reacted with atmospheric moisture [ref. 19 and references therein], whereas this reaction was avoided for pCOSIL by the hydrophobic nature of the host silicalite framework. Confined polymerization of CO in the channels of silicalite is thereby a unique way to obtain chemically stable pCO under normal conditions. In figure 2, we report the IR spectrum under ambient conditions of three different samples pelleted in free standing gaskets of comparable thickness, which were taken out of DACs and exposed to the atmosphere: (i) recovered, powdered pCOSIL, where also bulk pCO is present as a surrounding, embedding medium, (ii) pure bulk pCO synthesized at similar conditions, (iii) pure silicalite powder just pelleted in the gasket. We have focused on the C=O stretching region as other sections of the mid IR spectrum at lower frequencies are dominated by saturated peaks of the host silicalite framework. The composite IR peak of pCOSIL in the C=O spectral region can be considered to arise from the sum of three different absorption components and we have fitted the spectrum of pCOSIL using a linear combination of the experimental spectra of pure, bulk pCO and of pure silicalite and of an analytical, slightly asymmetric peak, which we assigned to the confined pCO. Indeed, the resulting fit is very good. Confined pCO can thus readily be identified by a single C=O stretching peak at 1758.5 cm^{-1}, whereas the composite band of bulk pCO is centered around 1739 cm^{-1}. Similar frequency shifts of 10-15 cm^{-1} between confined and bulk molecular materials in silicalite have been previously found in the case of dense CO_2 and C_2H_4, and they have been entirely assigned to the interaction of the confined molecules with the walls of silicalite[27,28]. The major point, however, is the very different spectral shape of the C=O stretching band between confined and bulk pCO. For bulk pCO the band is a composite one, as also found in all the IR spectra previously obtained on bulk pCO (ref. [19] and references therein). This composite band is most likely to be related to different kinds of carbonyl groups. In contrast to pCO obtained by polymerizing CO in the absence of confinement, pCO in pCOSIL exhibits a single peak, which is a strong sign of orientational and structural order. The slight asymmetry of this peak is probably an indication of strain, most likely related to confinement. Indeed, the ideal, infinite $[-(C{=}O)-]_n$ chain (fig. 1) has C=O groups pointing alternately in opposite directions in the asymmetric unit. The antisymmetric C=O stretching mode of these units is IR active, whereas the symmetric C=O stretching mode is Raman active. Therefore, the single C=O stretching peak in the IR spectrum is a strong signature for these ideal chains. Our DFT calculations show that the frequency of the symmetric Raman mode for this structural model is lower than the IR frequency by about 55 cm^{-1}, the splitting between the two modes being related to vibrational coupling. Measurements of the Raman peak were prevented by the strong photosensitivity and fluorescence emission of the whole mixture made of pCOSIL and the embedding bulk pCO around (see SI).

Single-crystal X-ray diffraction (SCXRD) measurements on pCOSIL have allowed us to determine the crystal structure of this unique composite material. This analysis was performed on the single pCOSIL crystal with the surrounding, amorphous bulk pCO, which was recovered from the gasket after the high-pressure synthesis and then glued on top of a glass fibre (fig. 3, inset). The crystal structure of pCOSIL was refined using the empty silicalite framework as a starting model in the orthorhombic space group *Pnma*. The refinement was stable giving an R factor of 13 %. Difference Fourier maps were obtained, Figure 3, which clearly show the presence of regions of diffuse electron density in both the linear and sinusoidal pores of the silicalite framework. This would be consistent with the presence of single, isolated, disordered pCO chains in both types of pores. Carbon atoms were added to the model in the positions corresponding to those of polyethylene in the silicalite/polyethylene nanocomposite with linear and sinusoidal carbon chains[28]. Refinements rapidly converged with an R factor of about 10 %.

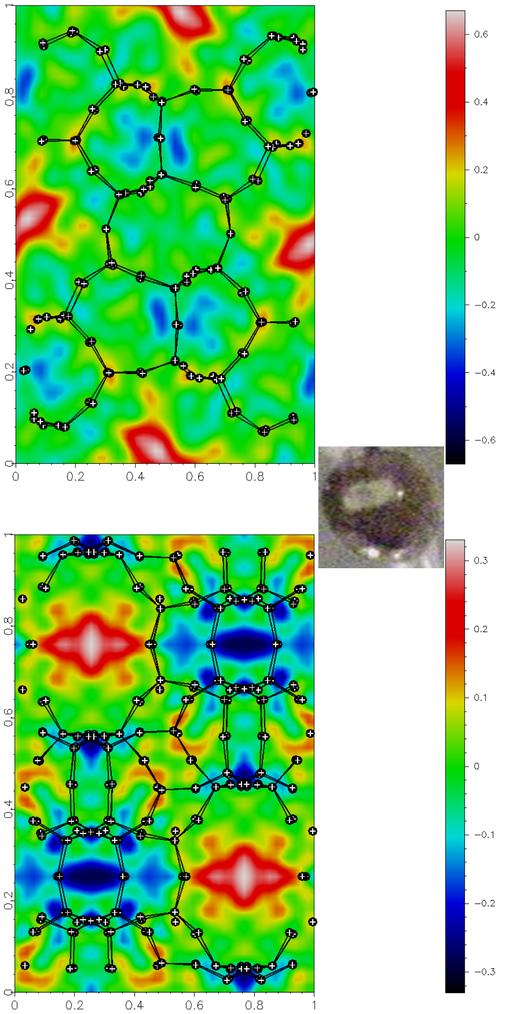

Figure 3. Difference Fourier maps of pCOSIL, showing the presence of regions of diffuse electron density due to C and O atoms in both the linear (top, orthogonal to the drawings) and sinusoidal (bottom) pores of the silicalite framework. Top (bottom) panel: projection along *b* (*a*). Inset: picture of the sample. A single pCOSIL crystal (lighter prism) is embedded in amorphous, bulk pCO (darker, round shaped material).

Two additional carbon atoms per asymmetric unit were added based on the strongest remaining peaks on the Fourier difference map. Due to the high degree of translational and conformational disorder in the confined pCO chain and the close scattering power of oxygen and carbon no real distinction could be made between carbon and oxygen atoms. However, based on the experimental IR results (see above) half of the guest atoms were defined as being carbon and the other half as oxygen, which had no effect on the R factor. This would correspond to 84 C/O guest atoms per unit cell. A final R factor of 9.2% was obtained corresponding to the structural model presented in Figure 4 (see also SI). If only one type of pore, linear or sinusoidal is occupied, the resulting R factor is close to 11 %. High atomic displacement parameters were obtained due to translational, orientational and conformational disorder of the polymer chains. The unit cell volume of the nanocomposite of 5351.5(5) Å^3 is consistent to that of unfilled silicalite (see also SI).

The combined IR and SCXRD results show that pCOSIL is made of a silicalite network and confined, extra-framework pCO chains, which are compatible with the ideal, *all-transoid* polycarbonil $[-(C=O)-]_n$ chains predicted to exist by DFT studies[20]. In our case, the pCO chains are highly strained due to the nature of spatial confinement. Indeed, there is translational and conformational disorder, the chains are bent in the sinusoidal channels of silicalite, and cross-linking between straight and sinusoidal pCO chains may occur at the junction of the corresponding host channels. All these reasons may easily prevent the predicted metallic nature of the pCO chains to occur in our real system. Synthesis of pCO in zeolites with linear 1D channel systems may allow such metallic polymers to be obtained in the future.

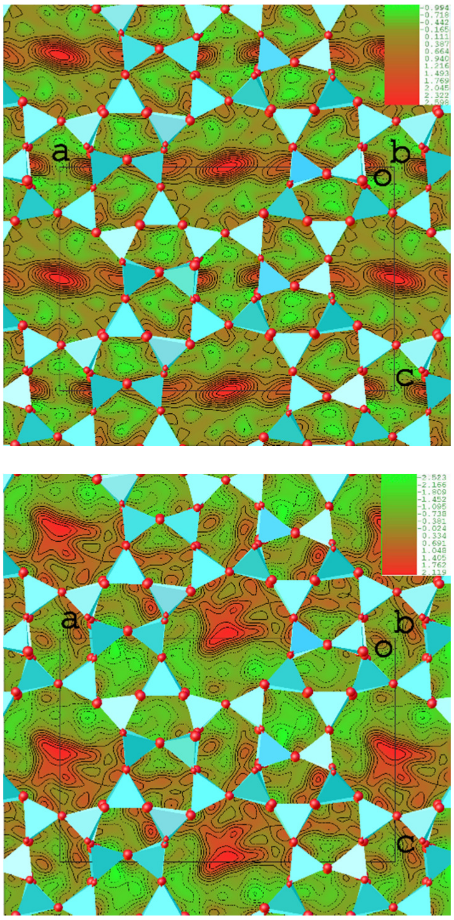

Figure 4. Structure of pCOSIL. Cyan tetrahedra and red balls: silicalite, SiO4 tetrahedra. Contour plots: charge density distribution for pCO in both the linear (orthogonal to the drawings) and sinusoidal pores of the silicalite framework. Top (bottom) panel: cut along the *b* axis at *y*=0 (y=1/4).

Our study is of paramount importance for fundamental and applied chemistry, as we have shown how strong confinement can affect self-assembly of simple, archetypal molecules in a dense state without the use of catalysts and/or radical initiators. Indeed, this type of confinement may affect the initial configuration of reactant monomers, in our case the mutual head-to-tail orientation of the CO molecules, along with the entire chemical pathway leading to the formation of confined polymers. Kinetic hindering of some chemical reactions can be overcome in this way and entirely new polymers can be obtained. One important aspect of polymeric CO, with obvious potential applications, is that it is a highly energetic, even explosive material[14]. Bulk pCO may be too unstable for easy handling and processing, i. e. for any practical applications. Strong confinement of pCO in an inert zeolite host could be a suitable protocol for making this important energetic polymer more stable and, as a consequence, more useful.

Associated Content

Supporting Information

Supplementary methods and materials, and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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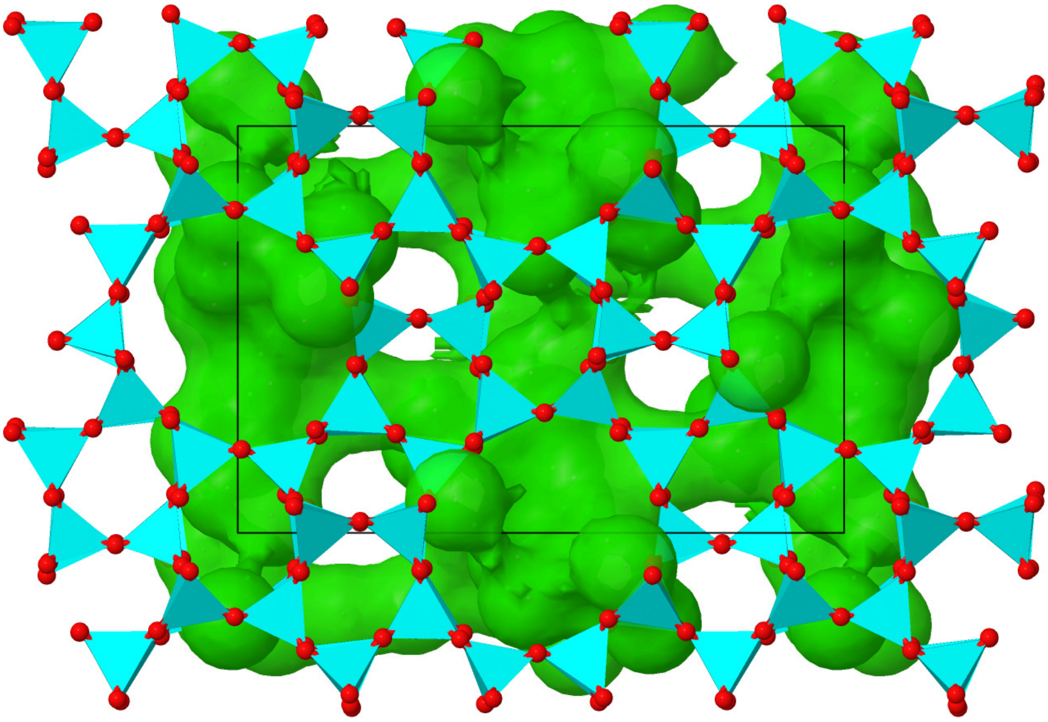
Table of Contents (TOC)



TOC. Projection of the polymeric CO/silicalite structure along the b-axis, with extra-framework, polymeric CO chains depicted according to their molecular surface.