Calorimetric study of CO condensed into mesoporous silica

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CO condensed into the 8 nm pores of SBA-15 porous silica has been studied by scanning calorimetry. The fractional filling has been varied. Melting/freezing as well as the α-β structural phase transition occurs at temperatures lower than in the bulk state and show hysteresis between cooling and heating. Either phase transition gives rise to a single, though broadened peak of the heat capacity, quite in contrast to previous results on H_2O and Ar in SBA-15, where the freezing anomaly is split into several components.

Molecular ensembles embedded in mesoporous silica substrates solidify and melt at temperatures well below the triple point temperature T_3 of the bulk state, an observation that is traditionally interpreted in terms of the Gibbs-Kelvin equation which relates the T shift to the inverse pore radius.[1] Furthermore there is considerable thermal hysteresis between freezing and melting. In case of complete pore filling (filling fraction $f=1$), both freezing and melting usually give rise to a single, although broadened peak of the heat capacity, which is of asymmetric shape with wide tails on the low-temperature (T) and a relatively sharp cutoff on the high-T side.[2]

Recent calorimetric studies on partially filled pores, $0 < f < 1$, have given further insight into the freezing/melting process in mesopores. The melting anomalies of partial fillings of Ar in Vycor glass,[3] H_2O,[4] and Ar (Ref. [5]) in SBA-15 are a little different from those of the completely filled case. However, the freezing anomalies have highly complex shapes and extend over quite a range of reduced temperature t, $t=T/T_3$. Most surprisingly, it is not in the highly random pore space of Vycor but in the rather homogeneous pores of the template grown substrate SBA-15, perhaps the most ideal mesoporous substrate available, that particularly wide and complicated freezing patterns have been observed. Thus the freezing of Ar in SBA-15 with a pore diameter D of 8 nm extends from $t=0.85$ down to $t=0.77$, with two relatively sharp peaks in addition to a broader component of the heat-capacity anomaly.

In somewhat simplified terms, our interpretation of the freezing/melting process is as follows:[3,5] For melting we favor an interfacial model according to which there is already well below the apparent melting temperature a liquidlike matching shell between the crystallized capillary condensate in the pore center and the pore walls. On heating, this shell grows in thickness and there is no need for other types of nucleation of the liquid state. On the other hand, the interfacial model predicts a wide T range of the supercooled metastable liquid states. Hence the actual growth of the solidified portion of the pore filling is controlled by the nucleation kinetics, which in turn depends on the arrangement of the pore filling in pore space. As will be discussed further below, the present results suggest some refinement of this view.

The present Brief Report deals with CO in SBA-15. As far the gas handling and the T range of interest is concerned, CO is a little different from Ar. There was no need for any change in the experimental setup and procedures; see Ref. [5]. In fact we even used the same substrate. We recall that the heating and cooling rates employed are 0.05 K/min, which is an order of magnitude smaller than what is usually possible with commercial scanning calorimeters. The partial fillings have been prepared in a well controlled way, namely, by condensing CO vapor into the pores at 70 K, in the liquid regime. The sorption isotherm is shown in Fig. 1. f is the uptake normalized to the uptake at the upper closure point of the adsorption/desorption hysteresis loop. The isotherm is quite similar to that of Ar (Ref. [5]) and Kr (Ref. [6]) in SBA-15; see Ref. [6] for a discussion of such isotherms.

We have chosen CO for the following reasons: In contrast to Ar, CO crystallizes in a noncubic crystal structure. We will exploit this point further below. Furthermore, CO shows an additional structural phase transition. As far as we know, there is no experimental information on such a phase transition for partial fillings.

In the bulk state, CO and N_2 are isomorphous.[7] They show a mesophase β with an hcp center-of-mass (c-o-m) lattice and orientational disorder of the molecular axes. The low-T α phase has an fcc c-o-m lattice; here the molecules are orientationally ordered in a four-sublattice fashion (space group $Pa3$). Bulk CO melts at $T_m=68.09$ K and the structural transition is at $T_{\beta\alpha}=61.55$ K. The entropy changes at the transitions are $\Delta S_m=1.476R$ and $\Delta S_{\beta\alpha}=1.237R$.[7] The latter entropy change is almost entirely due to the disordering of the orientations rather than to the fcc-hcp transformation of the c-o-m lattice.[8]

A previous study on CO and N_2 in the 7.5 nm pores of a silica xerogel[9] showed that the chemical potential in pores is
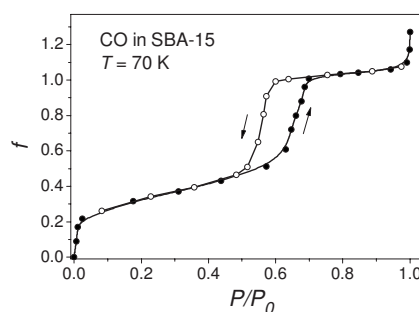

FIG. 1. Volumetric sorption isotherm (normalized uptake vs reduced vapor pressure) of CO in SBA-15, measured at 70 K.
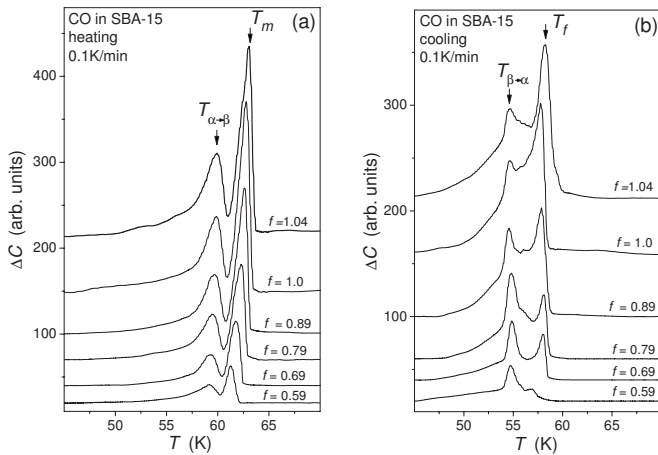
FIG. 2. The excess part of the heat capacity as function of temperature on heating (a) and on cooling (b). In order to avoid overlap, the curves are shifted vertically.

lower than in the bulk, both in the liquid and in the solid regimes. The phase sequence of CO is that of the bulk system on cooling, though with reduced transition temperatures, thermal hysteresis, and a lot of stacking faults in the c-o-m lattice. On heating out of the $Pa3$ low-T phase, the two aspects of the α-β transition, namely, the disordering of the orientations and the transformation of the c-o-m lattice, separate, giving rise to an intermediate orientationally disordered fcc phase. For pore confined N_2, the β-α transition is however suppressed. (This is why we preferred CO to N_2 for the present study.)

Eight fractional fillings of CO in SBA-15, prepared by adsorption at 70 K, have been investigated by scanning calorimetry, exploring temperatures between 40 and 70 K. The two samples with $f < 0.5$ do not show any heat-capacity anomaly. These data just serve as background for the anomalies that have been observed at higher f. Collective phase transitions leading to anomalies are reserved to the capillary condensed fraction of the pore filling. At least for freezing/melting, this observation has already been made in other studies on partially filled pores. The results on the anomalous part ΔC of the heat capacity are displayed in Fig. 2. The ΔC scale is arbitrary but the same for all samples. Two anomalies have been observed, both on heating and on cooling. Guided by the information on the bulk system[7] and on CO confined in the xerogel,[9] we assign them to the melting/freezing and to the α-β transition. "β" stands for the orientationally disordered mesophase of CO, independent of whether the c-o-m lattice is fcc or hcp, or whether there is even a further phase transformation between these structures; see Ref. 8.

Figure 3 shows the transition temperatures, taken at maximum $\Delta C(T)$, as a function of f. They are lower than in the bulk state and there is hysteresis between cooling and heating. The T shift is larger for freezing/melting than for the α-β transition. The T width of the β phase, ΔT_β, is 2–3 K only, compared to 6.5 K in the bulk state.[7] The values of $T_{\alpha \to \beta}$ and $T_{\beta \to \alpha}$ are very close to those observed in the xerogel.[9] The freezing and melting temperatures obtained in the xerogel are however higher ($T_f = 61$ K, $T_m = 64$ K), with the consequence that in the xerogel ΔT_β is close to the bulk reference value.
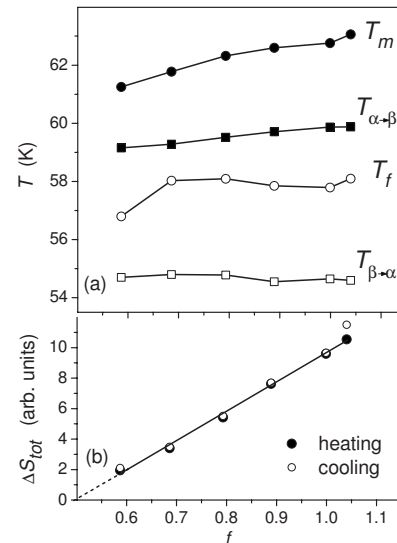

FIG. 3. The variations in the phase transition temperatures (taken at maximum heat capacity) and in the combined entropy change of the two transitions with the fractional pore filling.

The $\Delta C(T)$ data have been integrated in order to yield the anomalous part $\Delta S(T)$ of the entropy. ΔS_{tot}, the sum of the entropy changes at both transitions, is obtained by integrating over both anomalies, from 45 K up to temperatures of the liquid regime. As shown in Fig. 3, ΔS_{tot} is a linear function of f, proportional to $(f - f_c)$, with $f_c = (0.49 \pm 0.01)$. f_c compares favorably with the filling fraction at the lower closure point of the hysteresis of the sorption isotherm (Fig. 1). Thus ΔS_{tot} is proportional to the amount of capillary condensate present. The adsorbed film on the pore walls does not participate in the transitions.

In the bulk state, the melting and α-β transition contribute 55% and 45% to ΔS_{tot}, respectively.[7] In order to compare to this reference, $\Delta S(T)$ normalized to ΔS_{tot} for each individual value of f is plotted in Fig. 4. On heating, ΔC passes a deep minimum between the anomalies, at temperatures $T_\uparrow(f)$. Accordingly the $\Delta S(T)$ curves show relatively well defined plateaus that allow us to discriminate the entropy contributions of the two transitions, ΔS_m and $\Delta S_{\alpha\beta}$. In the cooling runs, the valleys between the ΔC peaks are less deep and the plateaus of $\Delta S(T)$ are practically absent. In order to separate the entropy changes at the two transitions on cooling, we split the integration range into two parts from 45 K to $T_\downarrow$ and from $T_\downarrow$ to 70 K. We examined various ways of how to choose $T_\downarrow$. Eventually we defined $T_\downarrow(f)$ as the temperature halfway between the peak temperatures T_f and $T_{\beta \to \alpha}$ and put pertinent markers (stars) on the $\Delta S(T)$ curves. The results to be described in the following depend little on the choice of $T_\downarrow$.

Compared to the bulk state, the entropy change at the α-β transition is enhanced at the expense of the freezing/melting transition, both for cooling and heating. Assuming that the molar entropy changes are equal or at least close to their bulk counterparts,[10] they can be translated into the temperature dependence of the liquid, α and β fractions of the pore filling. One arrives at the following conclusion: On heating up to $T_\uparrow$, the capillary condensate not only transforms from the α into the β phase, but a fraction of it has already melted,
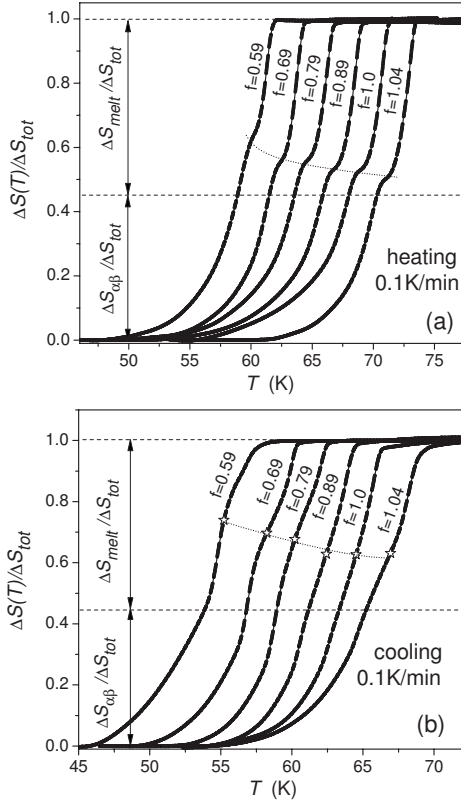
FIG. 4. The temperature variation of the excess entropy, normalized to the combined entropy change at both phase transitions, ΔS_{tot}, for each individual fractional filling. The temperature scale refers to $f = 0.59$. The data on the other fillings are replaced horizontally in steps of 2 K. The dotted and the dashed lines indicate the relative contributions of the two phase transitions in the confined and in the bulk states, respectively.

about 13% for $f = 1$ and 33% for $f = 0.59$. Compare the dotted line in Fig. 4 that connects the $T_\uparrow(f)$ data points with the $\Delta S_{\alpha\beta}/\Delta S_m$ partition of the bulk system.

On cooling, analogous observations can be made. Down to $T_\downarrow$, only a fraction of the capillary condensate solidifies, about half of it for $f = 0.59$ and about two-thirds for $f = 1$. The freezing of the liquid remaining occurs in the T range of the β-to-α transition. This view may be somewhat oversimplified, since the two anomalies overlap considerably; there are even minor features of $\Delta C(T)$ between T_f and $T_{\beta \to \alpha}$ that may indicate stepwise solidification.

Referring to reduced temperatures, relative to the bulk triple point, $t = T/T_3$, the freezing of Ar in the same substrate starts at $t = 0.85$ and extends down to $t = 0.77$.[5] For CO freezing starts at $t = 0.86$ and the β-to-α transition occurs at $t = 0.80$. Guided by the idea of corresponding states in CO and Ar, the comparison with Ar is another piece of evidence that on cooling some CO pore liquid remains down to $T_{\beta \to \alpha}$.

Thus there is evidence that the two phase transitions of CO in SBA-15 are characterized by broad regions of phase coexistence. Nevertheless either phase transition gives rise to just one peak of the heat capacity, quite in contrast to the previous results on partial fillings (Ar and H_2O in SBA-15, Ar in Vycor[3–5]), where the freezing anomaly is split into several components. In the following we comment on this

difference. For this purpose, we refer to two types of experimental results on other combinations of pore fillings and mesoporous substrates:

(i) Pores etched into (100) Si wafers are all aligned parallel. This allows the study of the crystallographic texture of the crystallized part of the pore filling. Complete fillings of Ar and N_2, solidified by cooling, give different results.[11] The diffraction pattern of Ar is that of an fcc powder. There is no texture. β-N_2 however shows a strong preference for the hexagonal c axis to be parallel to the pore axis. We have interpreted the texture arising in terms of the "selection-by-growth" mechanism that is exploited for the Bridgeman technique of single-crystal growth.[12] It relies on the anisotropy of the growth velocity and the geometry of the vessel. The pores of Si and of SBA-15 are both linear with extremely high length-to-diameter ratios. The results on Ar and β-N_2 in porous Si should also apply to Ar and β-CO in SBA-15.

(ii) The Bragg reflections of the two-dimensional (2D) triangular pore lattice of SBA-15 filled with liquid Kr have been investigated.[6] In the regime of capillary condensation, $f_c < f < 1$, the intensities vary with f in remarkably different ways for adsorption and desorption. The experimental data obtained for adsorption are consistent with a coexistence of completely filled pores and "empty" ones that have an adsorbed film of maximum thickness on the pore walls, but still vapor filled cores. We assume that this is a general property of molecular liquids condensed into the highly homogeneous pores of SBA-15.

With these two observations in mind, we interpret the different freezing scenarios of Ar and CO in SBA-15 as follows: The heat-capacity anomalies stem (almost exclusively) from the completely filled pores; see point (ii). The solid phase nucleates at several sites along a filled pore. The solidification fronts can propagate relatively freely along the pore. Eventually the advancing fronts emerging from different nuclei meet. For CO the c axes of the merging solidified pore sections coincide; the resulting grain boundaries are predominantly stacking faults with small interfacial energies. For Ar, where there is no such crystallographic texture, costly large-angle grain boundaries result, the formation of which the pore filling tries to avoid by keeping intermediate parcels of liquid that disappear only when the temperature is lowered further. The energies of grain boundaries depend on the crystallographic orientations of the grains in contact. One can imagine that the complex shape of the freezing anomaly of Ar reflects the distribution of grain-boundary energies. The same concept may apply to the freezing of H_2O in case pore ice had no preferred crystallographic texture with respect to the pore axis, which in turn is likely if pore ice were cubic rather than hexagonal.[13]

Following this line of reasoning, the β-CO solid in SBA-15 is in a highly ordered, almost single-crystalline state. The subsequent solid-solid transformation can then evolve practically in a single step. There are no major energy barriers that the advancing transformation front have to overcome.

This scenario refers to the phase coexistence along the pores. It has to be complemented by the radial coexistence with a matching layer between the core and the pore walls,

the thickness of which is T dependent. Pertinent models have been formulated.[3,14]

We have assumed that the all pores are equivalent and homogeneous. Thus there should be no variation in the transition temperature and the shape of the heat-capacity anomalies. The experimental data on fractional fillings from f =0.69 up to f=1 come close to this ideal situation. In fact, the span of the transition temperatures T_f, T_m, $T_{\beta \to \alpha}$, $T_{\alpha \to \beta}$ never exceeds 1 K and the shape of the anomalies changes little in this f range.

The samples with f=0.59 and f=1.04 require extra comments. For adsorption in the liquid regime, the onset of capillary condensation does not occur at f_c, as given by the lower closure point of the hysteresis loop of the sorption isotherm, but at a slightly higher f value, due to the supersaturation of the adsorbed film on the pore walls.[15] On cooling, the supersaturated part of the film will eventually delayer and solidify, at some temperature below the freezing temperature T_f of the capillary condensate that is present at higher f. For Ar in Vycor[3] and in SBA-15 (Ref. 5), this process leads to a further heat-capacity peak around 66 K. In the present system there is no such individual fingerprint of this process. Nevertheless T_f (f=0.59) is reduced with respect to the higher fillings (Fig. 3).

The slightly overfilled sample (f=1.04) has a vapor pressure that is still short of the saturated vapor pressure. Hence there is no bulk condensate around, consistent with the observation that there is no additional heat-capacity anomaly at T_3. The overfilling rather leads to a slight increase in T_m and in particular in T_f (Figs. 2 and 3). As discussed in detail in Ref. 5, we interpret this observation in terms of condensate residing in the pore mouths.

Motivated by the observation of rather complex freezing anomalies of pore confined Ar and H_2O, we have extended such calorimetric investigations to CO in SBA-15. The results on CO are in many respects of the conventional type. The transition temperatures, both of the freezing/melting and of the α-β solid-solid transition, are reduced with respect to the bulk reference and show thermal hysteresis. The heat-capacity anomalies have the usual asymmetric shape, as observed in many other pore condensates. The analysis of T dependence of the entropy change has been analyzed, giving evidence of a broad T range of phase coexistence. In particular, a part of the condensate stays liquid down to the β-α transition. The striking difference between the freezing processes of Ar and CO in SBA-15 was a special challenge to us. Guided by recent experiments on the texture of crystallized pore fillings, we suggest that the energy of grain boundaries has to be considered. Thereby the crystallographic texture of the solidified pore filling enters into the problem, which in turn depends on anisotropy of the crystal structure, whether, e.g., cubic or noncubic.

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