

ENTRAPMENT OF He AND Ne IN AMORPHOUS CARBON MOLECULAR SIEVE FIBERS

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Introduction

In our recent study, the sorption of He and Ne onto amorphous carbon molecular sieve fibers (CMSF) at atmospheric pressure and along the [295K, 77K] temperature range, was found to result in a reversible and efficient entrapment of these species by the solid micropores [1]. In that work, thermal programmed desorption mass spectrometry (TPD-MS) provided with a super molecular beam (SMB) inlet was used, showing that the effective dimension of the pore openings can be thermally regulated and adjusted to meet the critical dimensions of He and Ne, consequently allowing their highly selective admission. It was realized that such adjustments are achieved *via* two principal steps: (i) pore widening by means of an *irreversible* progressive removal of surface oxide groups upon evacuation at elevated temperatures and (ii) *reversible* regulation the *effective* pore opening via mechanism of thermal dilation. The above new insight into the entrapment mechanism established the status of pore closure versus temperature. Nonetheless, the interesting aspect of the physico-chemical nature of the entrapped gas remains unexplored. Aiming to gain insight into this open question, we were motivated to counter the problem by means of standard volumetric measurements. Our preliminary findings reveal abnormal dead volume values which are explained due to significant adsorption of He. Such results warrant the realization that entrapment phenomena occurring in microporous solids should be carefully noticed and considered to avoid significant erroneous determinations based on volumetric measurements.

Experimental

The CMSF sample was a ~100 mg fibrous cloth of TCM-128 (Carbone-Lorraine LTD, France). Sorption procedures for each gas (~1bar, 20/50 sccm UHP He /Ne), were carried out on the sample pre-evacuated at various temperatures, $T_0=100-500$ °C (with 100 °C intervals). For each combination of gas type and T_0 , two sorption procedures, differing in the temperature of gas introduction, were performed: (i) after stabilizing the sample's temperature to liquid nitrogen (LN_2), and (ii) *during sample cooling* from room temperature (RT) down to LN_2 . Sorption procedures were followed by removal of residual atmosphere by prolonged evacuation of samples at LN_2 . TPD-MS-SMB measurements [2] were performed by linearly (20 °C/min) ramping the sample temperature from LN_2 to T_0 . The desorbed products were probed with a Balzers QMG-422 quadrupole-mass spectrometer (QMS). According to the sorbed gas, the QMS signals $m/z=4$ and 20 were monitored versus T during temperature ramping. The above sorption procedures were strictly followed on duplicated samples in a standard high vacuum volumetric system, where the desorbed amounts were measured by collecting successive pressure portions of gas released into a calibrated volume. He and Ne adsorption isotherms were also performed for all samples under the same conditions.

Results and Discussion

Depicted in the left hand of fig. 1 are TPD profiles of He and Ne desorbed from the $T_0=100^\circ\text{C}$ CMSF sample. In contrast to the peaked solid curves corresponding to sorptions performed during sample cooling between RT and LN₂, the practically flat dotted curves, observed following sorptions taken at LN₂, confirm the occurrence of an entrapment phenomenon.

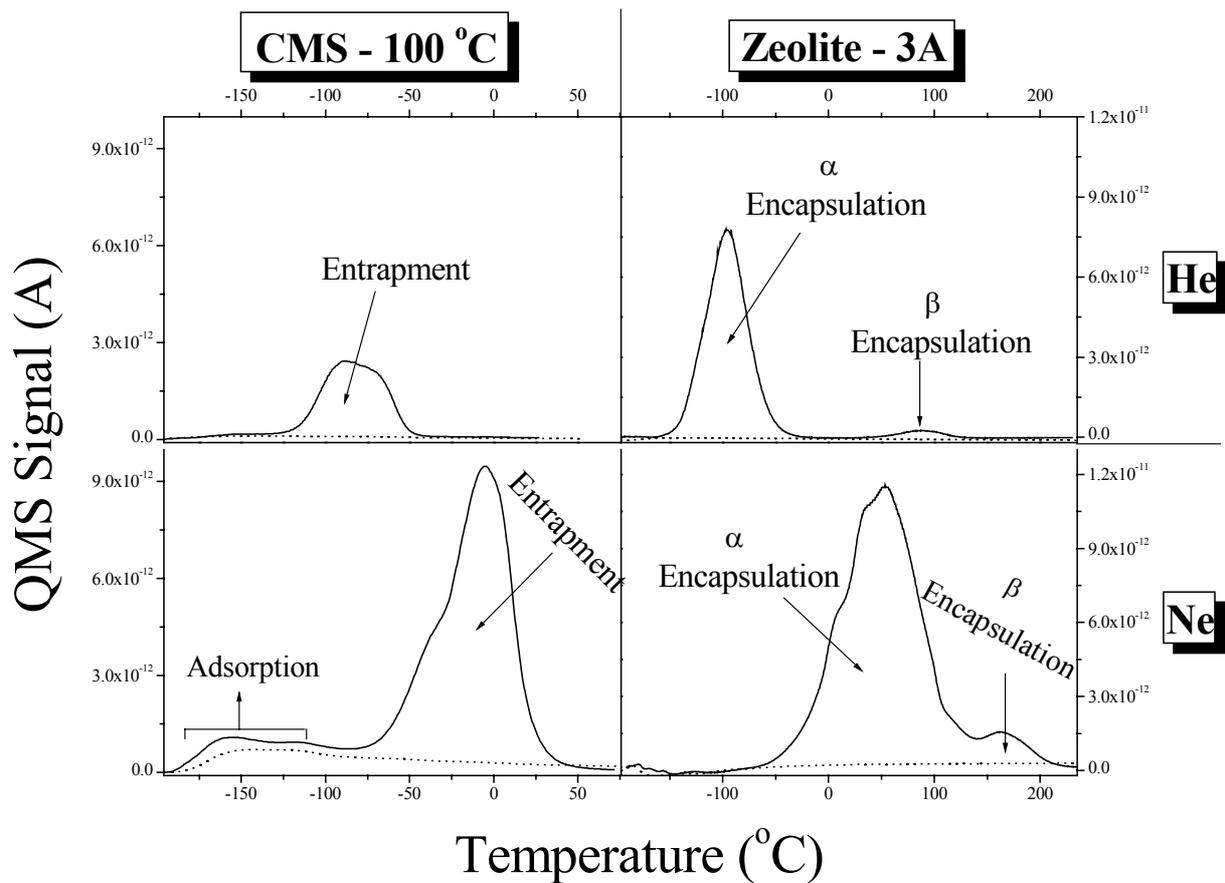


Fig. 1 TPD spectra of He (upper) and Ne (lower) from CMSF (left) and Zeolite 3A (right). Solid and dotted curves depict desorption spectra following sorption procedures performed during sample cooling (from RT and 573 K down to LN₂ for CMSF and Zeolite respectively) and at LN₂ respectively.

The evident difference between the He and Ne TPD profiles is in direct accordance with dimensional considerations of their effective diameter. Considering the entrapment phenomenon, the location of desorption peaks resemble activation energies required to dilate the pore opening so that the sorbed atom will be admitted through (and thus discharge from) the effective pore opening. Obviously the larger Neon atom, relative to He, necessitates larger opening of the pore in order to be admitted. This situation is evidently achieved at higher temperatures with respect to those sufficient for the admittance of the smaller He atom. The fulfillment of this expectation is experimentally revealed by the data of fig. 1 showing that while Ne discharges around 0°C, a temperature of ca. -100°C is sufficient for the release of entrapped He. This behavior persists for the remaining different T_0 CMSF samples, where increasing T_0 values systematically result in decreasing desorption temperatures [1]. This trend is interpreted as occurring due to a progressive increment of the effective pore opening following elevation of the evacuation temperature. The exact mechanism is discussed below.

It is interesting to mention that the above entrapment event in the amorphous solid is analogous to the encapsulation phenomenon recently observed in *crystalline* solids of regular cages network, occurring in the form of type A Zeolites [3,4]. The right hand side of fig. 1 depicts representative TPD spectra of He (upper) and Ne (lower) following sorption along cooling between 573 and 77 K. In that case the desorption peaks could be attributed to decapsulation from the □ and □ cages of the crystalline solid. The present observation of a similar phenomenon occurring in an *amorphous* solid is, by itself, interesting. The two phenomena, *entrapment* and *encapsulation*, are so termed to distinguish between confinement within amorphous constriction and inside crystalline cages of regular cavity structure respectively.

In either case, reversible thermal dilations of the framework/constrictions play a major role in determining the effective aperture/pore opening of the zeolite/CMSF. In the case of CMSF, another, *irreversible*, temperature dependent sub-mechanism governs the admittance/entrapment of He and Ne. The pre-evacuation treatment at various temperatures, removes surface oxides, consequently widening the pore opening. The higher the evacuation temperature, the larger extent of removed surface oxides. Cooling to LN₂ contracts the pore aperture to various extents of practical pore enclosure, in accordance with the pre-evacuation value of T_0 . The overall accumulated data shows that higher evacuation temperatures remove surface oxides more efficiently to such extents that closure of the pore opening following cooling to LN₂ evidently becomes less effective. In the case of He, for example, a situation of a total ineffective closure is attained for $T_0 = 400$ °C, whereas for Ne, for $T_0 = 500$ °C still results in a relative fair effective pore closure at LN₂ [1].

An insight into the physico-chemical nature of the entrapped gas was provided via volumetric measurements by utilizing the results of the TPD experiments. As received CMSF samples were pre-evacuated at two extreme temperatures: (1) 500 °C, for which TPD data indicated the highest extent of pores opening, for which full gas access is possible even at temperature as low as LN₂, and (2) 100 °C for which the TPD data indicated completely blocked pores at LN₂.

Ne isotherms could be solely obtained for samples pretreated at high T_0 values, i.e. only those possessing widely opened pores. In those cases significant amount of adsorbed Ne was indicated. Due to the use of He as the dilatometric fluid, the

performance of comparative He isotherms is meaningless. Nonetheless, in the case of He, dead volume measurements were performed at LN₂, resulting in abnormal dead space values which clearly indicate He adsorption at LN₂. Samples of low T₀ values, i.e. those possessing insufficient gas accessibility into the free pore volume, acted as inert substances indicating of practical null adsorption, where no detectable amounts of adsorbed He could be deduced. In marked contrast to the above, dead volume measurements on high T₀ samples, resulted in anomalous values exceeding even the volume of the empty calibrated volume containing the sample. A principal conclusion thus emerges, where He, the most inactive and the least adsorptive gas onto solids, shows considerable adsorption onto the exposed inner surface of CMSF pores. A similar behavior was observed [5] and is currently studied for the case of He confined within the inner free volume of Zeolitic cages. As for the entrapped gas, conclusive data on its physico-chemical nature at T > LN₂ is nontrivial, requiring additional detailed experiments to be performed.

Conclusions

By utilizing new data from recent entrapment experiments of He and Ne in carbon molecular sieve fibers, it was confirmed that He is considerably adsorbed onto the inner surface of the CMSF pores. Such a result should warrant the realization that entrapment phenomenon occurring in microporous solids should be carefully noticed and considered to avoid significant erroneous determinations based on volumetric measurements. Careful attention must also be given to the thermal history of such substances.

References

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