Video Article

Supercritical Nitrogen Processing for the Purification of Reactive Porous Materials

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Abstract

Supercritical fluid extraction and drying methods are well established in numerous applications for the synthesis and processing of porous materials. Herein, nitrogen is presented as a novel supercritical drying fluid for specialized applications such as in the processing of reactive porous materials, where carbon dioxide and other fluids are not appropriate due to their higher chemical reactivity. Nitrogen exhibits similar physical properties in the near-critical region of its phase diagram as compared to carbon dioxide: a widely tunable density up to ~1 g ml^{-1}, modest critical pressure (3.4 MPa), and small molecular diameter of ~3.6 Å. The key to achieving a high solvation power of nitrogen is to apply a processing temperature in the range of 80-150 K, where the density of nitrogen is an order of magnitude higher than at similar pressures near ambient temperature. The detailed solvation properties of nitrogen, and especially its selectivity, across a wide range of common target species of extraction still require further investigation. Herein we describe a protocol for the supercritical nitrogen processing of porous magnesium borohydride.

Video Link

The video component of this article can be found at https://www.jove.com/video/52817/

Introduction

Supercritical fluid extraction (SFE) and drying (ScD) methods are well established in a wide range of practical applications, especially in the food and petroleum industries, but also in chemical synthesis, analysis, and materials processing.[1-6] The use of drying or extraction media at conditions above their critical points is often faster, cleaner, and more efficient than traditional (liquid) techniques, and has the added advantage of being highly tunable with respect to the solvation power of the fluid by slight adjustment of the operating conditions.[3,7] A simple ScD method consists of three basic steps. The first step is exposing the solid (or perhaps liquid) starting material which contains the target impurity compound to an appropriately chosen ScD fluid in its liquid (or near-liquid supercritical) phase, where its high density corresponds to a high (and perhaps selective[7]) solvent power with respect to the target species. The second step is heating and compressing the system above the chosen ScD fluid's critical point in a closed container so that the fluid and its dissolved target species do not pass a phase boundary which might result in separation. The final step is slowly reducing the pressure of the ScD fluid to vacuum at a temperature above the critical temperature, allowing the fluid solution containing the target species to escape, again without encountering a phase boundary or any detrimental surface tension effects along the way.

The starting material is left depleted of the target species and may be subjected to iterated treatments if necessary. In cases of supercritical fluid extraction, the target solute species is the desired product, and is collected from solution for further use.[8,9] In other cases, the dried or purified starting material is the desired product, and the extracted impurities are discarded. This latter scenario, referred to herein as the ScD approach, was discovered to be an effective strategy for the pretreatment of high surface area, microporous materials such as metal-organic frameworks (MOFs), where traditional heat-treatment methods under vacuum are in many cases not sufficient in clearing the pores of all unwanted guests, or result in pore collapse.[10] Carbon dioxide ScD (CScD) processing is now a routine post-synthetic process for MOFs,[11] leading to increases in nitrogen-accessible surface areas over untreated materials of up to 1,000%[12] and other improvements, such as in catalytic activity.[13] Other notable supercritical fluid applications are as a widely tunable medium for chemical reactions,[14-16] supercritical fluid chromatography (SCFC)[6,17,18] and synthesis of aerogels and advanced composite materials.[19-22]

For drying applications, a ScD fluid is chosen based on two criteria: a) the proximity of its critical point to ambient conditions (for convenience and to reduce energy costs or process complexity) and b) its solvation power with respect to the target species. Carbon dioxide (CO_2) has proven to be a convenient ScD fluid in many applications since it is nontoxic, nonflammable, and cheap, and can be tuned to exhibit a high solvation power toward a number of common organic target species in its near-liquid state (at pressures of <10 MPa and temperatures of 273-323 K).[1-3,7-9] Other common supercritical solvents (or co-solvents) include water (spanning a remarkable range of solvent properties

between its ambient and supercritical state[23]), acetone, ethylene, methanol, ethanol, and ethane, covering the spectrum from polar (protic and aprotic) to nonpolar, and having critical points relatively near to ambient conditions.

Carbon dioxide is by far the most common ScD fluid used. In established CScD methods, the reactivity of the starting material is not an inhibitive factor since CO_2 is only very weakly reactive at temperatures near its critical point. However, certain classes of materials such as so-called complex hydrides (*e.g.*, alanates and borohydrides) present unique challenges in handling due to their strong reactivity in the presence of water or CO_2 in addition to their (perhaps intentionally tailored) instability under heating.[24-26] Moreover, there is great international interest in such materials as high-density hydrogen storage compounds,[27-30] and therefore also in nanostructured and/or porous varieties[31-33]. For the effective purification of such reactive, unstable, and nanostructured materials, ScD methods are a promising strategy.[34] A ScD fluid must be used which has a small molecular diameter appropriate for penetration into narrow cavities and which also has a high solvation power toward the target impurities, while remaining unreactive toward the starting material itself. Herein, the use of supercritical nitrogen (N_2) as an effective fluid for such extraction and especially drying applications is presented. A specific supercritical nitrogen drying (NScD) methodology is described below for the purification of γ-phase magnesium borohydride where the target species include both diborane and an *n*-butyl compound (similar to but not specifically identifiable as *n*-butane). The following protocol can be easily modified for general extension to other supercritical nitrogen drying or extraction processes.

Protocol

1. Apparatus

1. Use a basic supercritical drying (ScD) apparatus comprised of four primary components connected by high pressure gas tubing: the gas supply, a vacuum system, sensors (temperature and pressure), and the sample environment (which can be submersed in a bath). Ensure that the construction is of high-quality stainless steel valves, fittings, and tubing, pressure-rated to at least 10 MPa within the temperature range between 80-300 K.
Note: A schematic is shown in **Figure 1**.
2. For nitrogen ScD (NScD) treatments, ensure that the gas supply is research purity (>99.999%) nitrogen gas fitted with a pressure regulator for outlet pressure control between 0-10 MPa. Attach a 50 L bottle (20 MPa) to the apparatus, and purge the system with pure nitrogen multiple times before use.
3. Ensure that the vacuum system is capable of achieving vacuum pressures down to <0.1 Pa and is connected to the apparatus with a fine-control needle valve. Preferably, use an oil-free roughing pump and a molecular-drag turbo pump, placed in series.
4. Use at least two pressure sensors for accurate measurement of the pressure during ScD treatments: a low pressure sensor for vacuum measurement and a high pressure sensor to achieve a total measurable pressure range between $0.1\text{-}10^7$ Pa.
5. Use at least two temperature sensors for the minimal accuracy necessary to perform typical ScD treatments: a sensor in thermal contact with the sample and a sensor within the primary gas dosing manifold for accurate measurements between 77-300 K (*e.g.*, K-type thermocouples).
6. Check that the sample holder has an appropriate inner volume to contain the amount of sample necessary for treatment, and is constructed of stainless steel.
Note: A lengthened cylindrical design aids in thermal contact with the bath.
7. Ensure that the fitting that closes the sample container is appropriate for high pressures and repeated use (*e.g.*, Swagelok VCR). Connect the sample container volume to a valve for isolation from the outside environment via an appropriate length of tubing (the dip tube) for complete immersion of the sample holder into the bath.
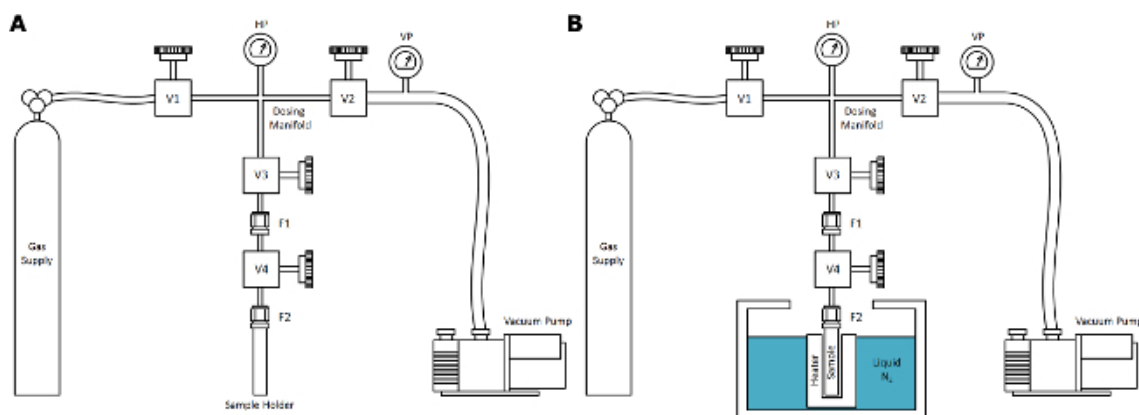

Figure 1. Supercritical Nitrogen Drying (NScD) Apparatus. A schematic depiction of the simplified NScD apparatus for use in the typical laboratory: (**A**) at ambient temperature and (**B**) after submersion of the sample in the bath. The gas supply for the process described in this work is nitrogen, but this general apparatus is generalizable to other ScD fluids with a critical point lying within a practical range of temperature and pressure, such as CO_2. The components are labeled for consistency with the protocol described herein. Please click here to view a larger version of this figure.

2. Preparation

1. Load 0.2-0.5 g of sample (γ-Mg(BH$_4$)$_2$, in powder form, following wet-chemical synthesis and standard drying methods) into the sample holder under appropriate conditions, typically in an inert atmosphere such as an argon glovebox, at ambient temperature or below. Close the sample holder (fitting F2) with a filter gasket and then close the valve (valve V4). Transfer the sample holder to the apparatus and attach (fitting F1).

2. Open the dosing manifold to vacuum via V2 and evacuate. Open V3 and evacuate. Purge the apparatus with nitrogen via V1 and evacuate via V2. Open V4 and evacuate the sample at RT for up to 24 hr, to reach the minimum pressure of the system (<0.1 Pa).
3. Install the sample bath (see **Figure 2**) around the sample holder. Perform this by raising the bath into position on a scissor lift, or similar mechanism.
4. Set the heater to the desired future liquid temperature (T_l, see step 3.1) of 110 K, and continue to evacuate the apparatus until the temperature equilibrates.
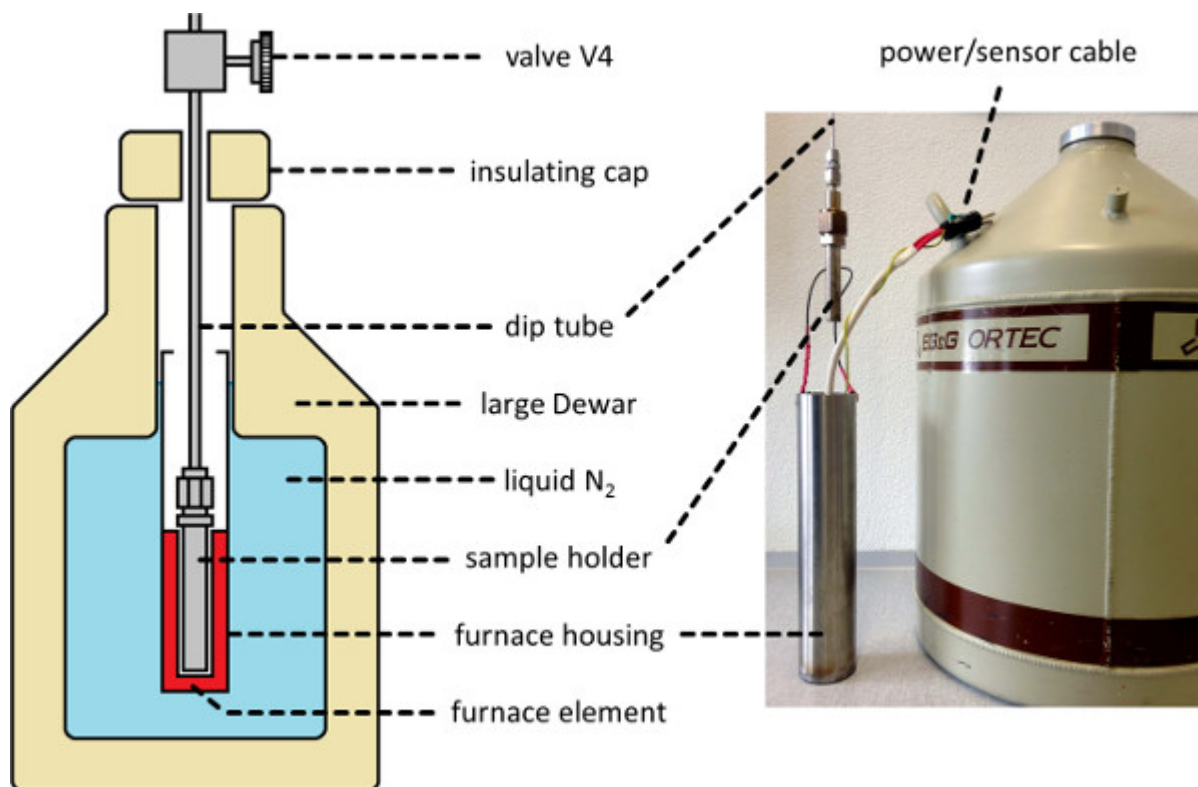

Figure 2. Cryogenic Furnace Sample Bath. A schematic depiction (left) and photograph (right) of a cryostatic thermal bath environment appropriate for containing the sample holder during NScD processing, permitting measurement and control of the sample temperature between 77-298 K. Please click here to view a larger version of this figure.

3. Supercritical Nitrogen Exposure

1. For NScD processing of γ-Mg(BH$_4$)$_2$, (the subject of demonstration in this protocol) select a liquid temperature (T_l) of 110 K. This corresponds to a moderate liquid solvent density (~0.6 g ml^{-1}); Adjust as necessary for the application of this protocol to other NScD treatment processes (see the Note below).
2. Close off the system to vacuum by closing V2. Throttle open V1 slowly, allowing the pressure to increase into the liquid region of the phase diagram. Equilibrate the system at 2 MPa and T_l.
3. Soak the sample in liquid N$_2$ for 4 hr.
4. Set the heater to 150 K with a ramp ≤2 K min^{-1}. Allow the pressure to increase no higher than the maximum rated pressure of the apparatus (this P$_{max}$ should be ≥10 MPa); if necessary, carefully vent the excess pressure to vacuum via V2. Equilibrate the system at P$_{max}$ and 150 K.
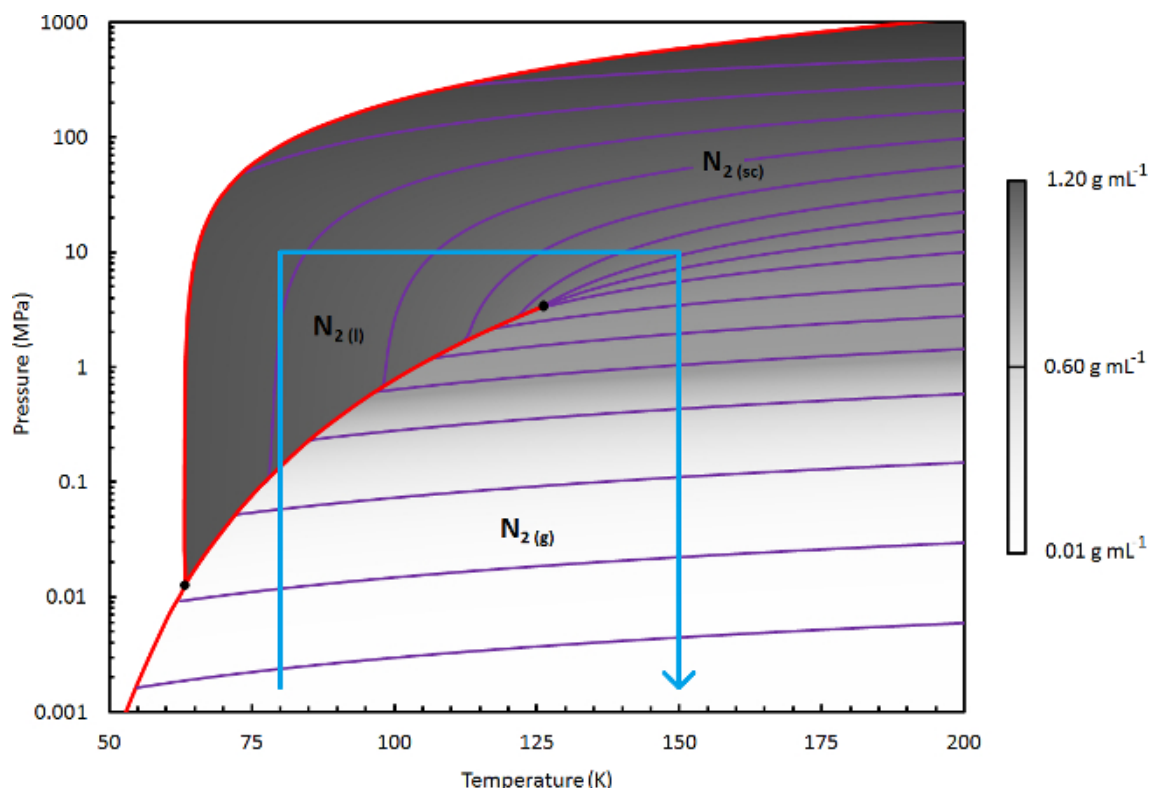5. Soak the sample in supercritical N$_2$ for 1 hr.

Figure 3. Phase Diagram of Nitrogen. A detailed phase diagram of nitrogen, where the fluid density (shown in linear greyscale) is calculated using Refprop (a modified Webb-Benedict-Rubin equation of state).[41] Various lines of constant density are shown in purple. The solid phase boundaries and boiling transition lines are shown in red. The blue lines indicate the boundary of the region of the phase diagram that is relevant for drying or extraction processing using N_2. Please click here to view a larger version of this figure.

Note: For the application of this protocol to other materials, establish an appropriate NScD treatment scheme by choosing the conditions necessary for effective solvation of the target species. Refer to the phase diagram of N_2, shown in **Figure 3**. To achieve a high fluid density in the liquid phase (*e.g.,* 0.8-1 g ml^{-1}), select a T_l of 80-90 K. For moderate liquid density (*e.g.,* 0.6-0.8 g ml^{-1}), select a T_l of 90-115 K. A trial and error approach may be necessary.

4. Supercritical Nitrogen Release

1. Carefully crack the system to vacuum by throttling V2, allowing the pressure to decrease as slowly as possible. Repeatedly crack the system to higher vacuum rates as necessary to achieve a gradual decline to high vacuum (<0.1 Pa) in the approximate time span of 12-24 hr.
2. Remove the sample bath and fully open V2 to completely evacuate the sample. Equilibrate at RT and high vacuum (<0.1 Pa).
3. Degas the sample at RT and <0.1 Pa for 1-24 hr, as desired.

5. Post Treatment

1. Close valves V3 and V4, and remove the sample holder from the apparatus (fitting F1).
2. Transfer the sample holder to an inert environment for handling, such as an argon-filled glovebox. Remove the sample from the sample holder (fitting F2) and store in a sealed container at ambient temperature or below.

Representative Results

Alkali and alkaline earth metal borohydrides are potential hydrogen storage materials, which deliver a large content of gaseous hydrogen upon decomposition.[27,29] Other decomposition products such as diborane have also sometimes been detected in the gas desorbed, but their origin is not a priori clear; it is possible they are products of the pure phase decomposition, but may also be impurities or products of reactions of impurities leftover from chemical synthesis.[35] The porous phase of magnesium borohydride (γ-Mg(BH$_4$)$_2$) exhibits both a high specific surface area (>1,000 m^2 g^{-1}) and a very high gravimetric (14.9 mass%) content of hydrogen.[36] Its enthalpy of dehydrogenation is experimentally reported to be between 40-60 kJ mol^{-1},[37] an intermediate value that is close to ideal for hydrogen storage at near ambient conditions[38]. Due to its very purpose as a moderate temperature hydrogen storage material, γ-Mg(BH$_4$)$_2$ cannot be heat-treated and degassed at elevated temperatures in an analogous way to other microporous materials such as activated carbons or aluminosilicates. In addition, common ScD techniques such as with CO$_2$ are also inapplicable since Mg(BH$_4$)$_2$ (as other borohydrides[25] and alanates[26]) is well known as a powerful reducing agent that reacts with CO$_2$ under even mild conditions. This was reported to occur after exposure at 313 K and 9 MPa in our recent work[34] and even as low as at 303 K and 0.1 MPa in other recent work[39].

We subsequently reported[34] that the supercritical N_2 drying (NScD) methodology described herein was successful for the purification of γ-$Mg(BH_4)_2$. This was found to be a decisive strategy for the quantification of its true hydrogen storage content upon decomposition up to 593 K, and may also be crucial for the correct determination of the reaction route and intermediates: that is, in the absence of impurities that can significantly alter the pathway of decomposition. The target species of extraction were identified to be diborane (B_2H_6) and an unspecific *n*-butyl impurity (likely to be $Mg(Bu)_2$ or a fragment thereof), in the initial concentrations of 1.9 and 1.2 mass%, respectively. The NScD protocol described above was applied in 1x-3x iterations, and the resulting materials were compared to the untreated product following the standard synthesis routine including the final evacuation step under vacuum at 353 K. Both impurities were found to be reduced to negligible quantities (below 0.1 mass%, the detection limit) after 3x-NScD treatments (*e.g.*, see **Figure 4**). In this way, pure H_2 was found to be the only gaseous product of decomposition of γ-$Mg(BH_4)_2$ under the conditions employed. The crystal structure of the starting material was not affected by NScD treatment, and nitrogen-accessible surface area was found to substantially increase. Further, the decomposition pathway of the porous phase appeared to have been altered after the removal of impurities in that it proceeded via a continuous structural degradation (amorphization or collapse)[34] instead of via the normal series of transitions between a number of higher temperature crystalline phases[40], indicating that control of the impurities present during decomposition is crucial for accurate analysis of this reaction.
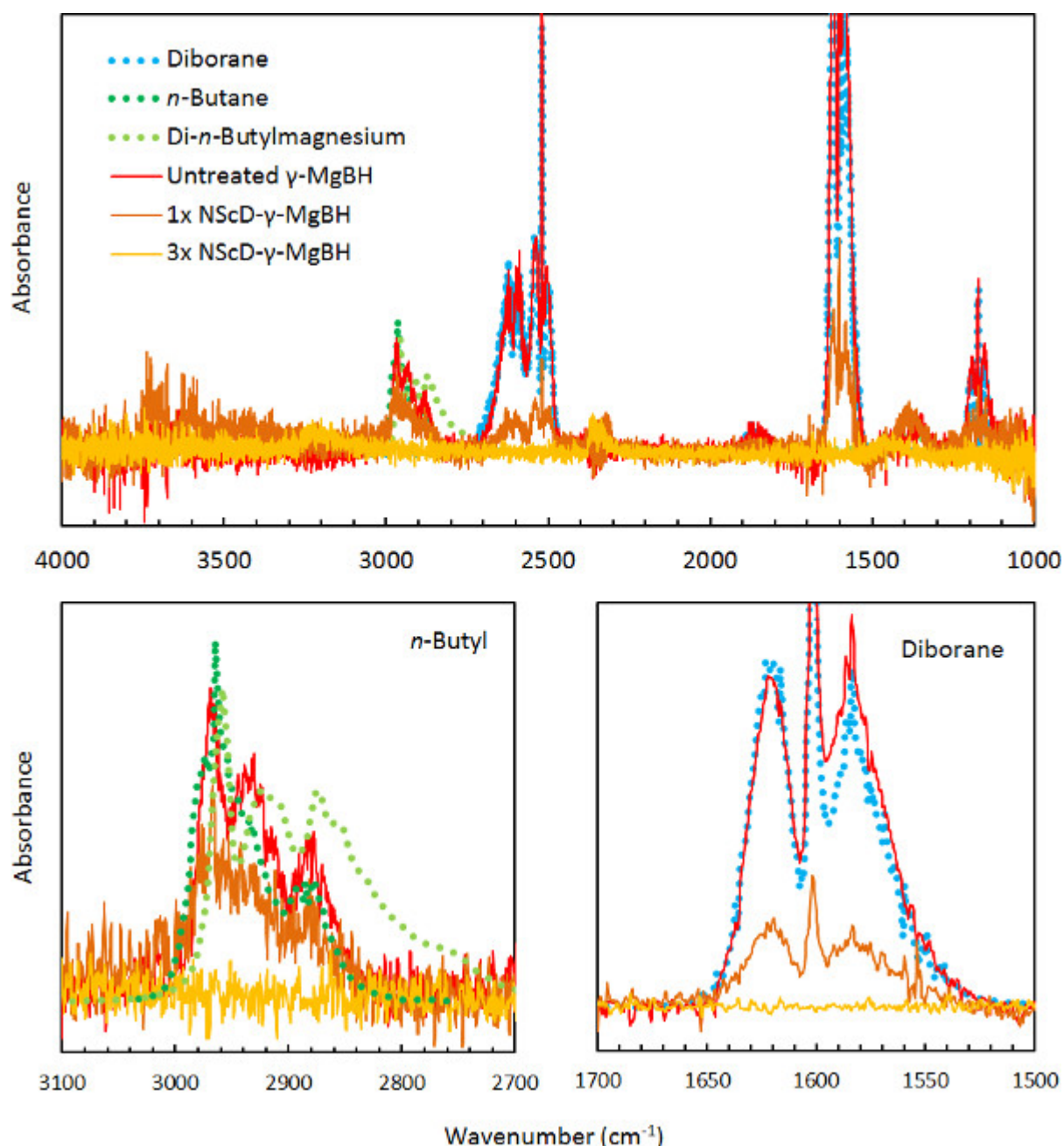
Figure 4. Infrared (IR) Spectra of the Gaseous Decomposition Products of γ-Mg(BH₄)₂. Thermal decomposition of γ-Mg(BH₄)₂ was performed under flowing H_2 at 400 K and 0.1 MPa. The untreated material shows a significant release of diborane (bottom right) and n-butyl impurities (bottom left) which are sequentially reduced upon iterated treatments with NScD (1x and 3x iterations shown here). The units of IR absorbance (y-axis, not shown) are normalized with respect to the quantity of starting material. Please click here to view a larger version of this figure.

	N_2	CO_2
Critical Temperature (K)	126	304
Critical Pressure (MPa)	3.4	7.4
Critical Density (g ml⁻¹)	0.31	0.46
Practical Liquid Temperature (K)	77	273
Practical Liquid Density (g ml⁻¹)*	0.81	0.93
Kinetic Diameter (Å)	3.6	3.3

Table 1. Comparison of ScD Fluid Properties of Nitrogen and Carbon Dioxide.

Discussion

Perhaps due to its relatively low critical temperature (126 K), N_2 has historically been overlooked as an effective ScD solvent. In earlier reports,[3,17,42,43] it has only been alluded to in the context of processing temperatures at or above ambient, where it exhibits only modest solvation power due to its low fluid density in this region of its phase diagram (except at extremely high pressures[43]). The key step in realizing the practical utility of N_2 as a supercritical solvent is in maintaining a treatment temperature near the critical point, where the density (and therefore solvation potential) is an order of magnitude higher than at ambient conditions: 0.3 g ml^{-1}, ~40% that of liquid N_2. To its advantage, N_2 has a similar kinetic diameter[44], critical density[41], and critical pressure[41] to CO_2, and its critical temperature is accessible in a typical laboratory with the use of liquid nitrogen as a coolant (see **Table 1**). Further, N_2 is also cheap, nontoxic, and completely nonflammable, similar to CO_2. While both CO_2 and N_2 exhibit a non-zero quadrupole moment, N_2 is considerably less quadrupolar, indicating some advantages for N_2 toward nonpolar target species (*e.g.*, alkanes). A comparison of the phase diagrams of CO_2 and N_2 is shown in **Figure 5**.
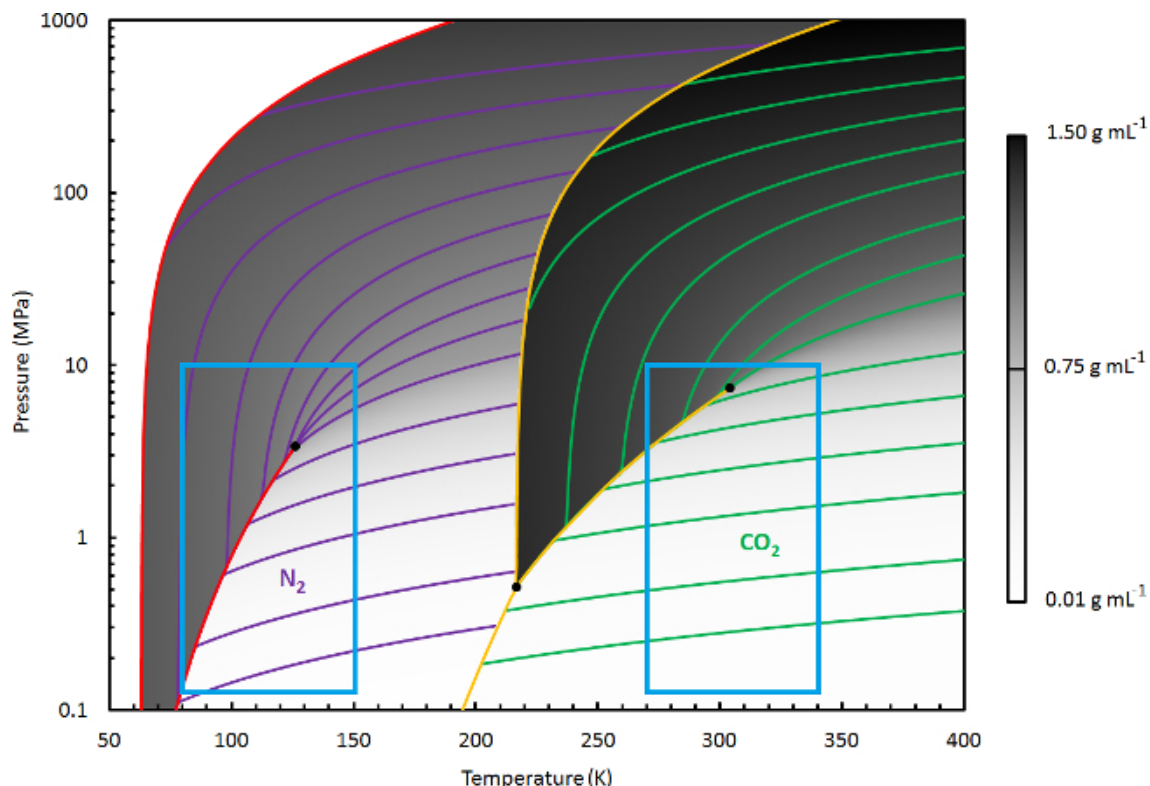

Figure 5. Phase Diagrams of Nitrogen and Carbon Dioxide. The overlaid phase diagrams of nitrogen and carbon dioxide, where the fluid density (shown in linear greyscale) is calculated using Refprop (as in **Figure 3**).[41] Various lines of constant density are shown in green for CO_2 and purple for N_2. The solid phase boundaries and boiling transition lines are shown in yellow for CO_2 and red for N_2. Two blue boxes indicate each region of the phase diagram that is typically relevant for drying or extraction processing using CO_2 (right) and N_2 (left, described in this work), respectively. Please click here to view a larger version of this figure.

The supercritical nitrogen (NScD) processing techniques described herein are generally applicable to the purification and physical activation of any porous material, but are especially relevant to materials that are both narrowly microporous and potentially reactive or unstable under otherwise mild treatment conditions. Presently, this class of materials is small but growing (*e.g.*, γ-Mn(BH$_4$)$_2$ has been recently reported[45]) due to great international interest in nanostructured energy storage materials that have a characteristic temperature of stability that is close to ambient and which are strongly reactive, ruling out CScD techniques. The hydrogen storage community, and especially those preparing novel (porous or nanostructured) borohydride or alanate compounds, can perhaps benefit most presently from the use of NScD processing methods in purifying the products of wet synthesis where complete solvent removal is a difficult task. Other materials of potential relevance are reactive metal-organic frameworks (and related coordinated framework materials) or their functionalized variants, and other sub-classes of materials that may not be presently well known simply because obtaining them in the pure state has been unsuccessful with CScD and other solvent removal methods.

It should also be noted that strongly reactive materials such as complex hydrides are not only difficult to purify directly following wet chemical synthesis, but are also inherently likely to be continuously contaminated during storage. Handling these materials without significant accumulation of impurities is a great challenge, and the analysis of "fresh" samples is often emphasized. Processing such materials using NScD techniques is likely to be an effective solution. While the specific solvation power of N_2 toward a wide range of commonly targeted species of chemical extraction methods is not well investigated in the near-critical region of its phase diagram, it is expected that its solvation power and selectivity, especially toward small nonpolar molecules, is easily tunable as in other ScD fluid systems. The differences between N_2 and CO_2, and the interplay between N_2 and other co-solvents, in the relevant region of the phase diagram for NScD processing remains to be explored.

The most important limitation of the NScD methodology may be its requirement of near-cryogenic temperatures, hindering its practicality for large-scale industrial applications. While liquid nitrogen remains a very cheap coolant (*e.g.*, ~0.2 USD per L), any process taking place under such wide temperature swings as NScD methods is costly. In addition, while nitrogen is a relatively inert compound, there are materials which are known to react with N_2, even at ambient or near-ambient conditions (*e.g.*, lithium). Clearly, materials with pores that are too small to host N_2 molecules will not be applicable for NScD processing. Lastly, it should be noted that while the density of liquid and near-liquid supercritical nitrogen can approach values of ~1 g ml^{-1} (*e.g.*, ρ_{N2} = 0.9 g ml^{-1} at 60 MPa and 80 K), the very high pressures required to achieve such high solvent densities make the NScD methodology rather unattractive for applications that demand extremely high solvent power. In comparison, such solvent densities are much more easily achieved with carbon dioxide when the possibility of cooling the liquid CO_2 to temperatures below 273 K is considered (*e.g.*, ρ_{CO2} = 1 g ml^{-1} at 0.6 MPa and 220 K) making the CScD methodology an extremely versatile method for drying or extraction processes for all porous materials except those which are reactive toward CO_2. Other inert supercritical solvents such as argon[46] may also be of interest for the purification of reactive, porous materials.

Disclosures

The authors have nothing to disclose.

Acknowledgements

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