In Situ Switching of Sorbent Functionality as Monitored with Hyperpolarized ^{129}Xe NMR Spectroscopy[†]

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Abstract: In this contribution, we demonstrate that a material (organic zeolite mimetic coordination polymer [CuL_2], where L = L^- = $CF_3COCHCOC(OCH_3)(CH_3)_2$) can be endowed with its functionality in situ under molecular-level control. This process involves the isomerization of the ligands followed by phase interconversion from a dense to an open, porous form. The porous (β) form of the complex reveals zeolite-like behavior but, unlike zeolites and many other hard porous frameworks, porosity may be created or destroyed at will by the application of suitable external stimuli. Contact with methylene chloride vapor was used to switch on the sorbent functionality, whereas switching off was accomplished with a temperature pulse. The transformations between functionally inactive α and active β forms, as well as the amount of vacant pore space, were monitored in situ by observing the NMR spectrum of hyperpolarized (HP) Xe atom probes. For methylene chloride, the chemical shift of the coabsorbed HP Xe correlated directly with the amount of adsorbate in the pore system of the open framework, illustrating the use of HP Xe for following sorption kinetics. The adsorption of propane, as an inert adsorbate, was also monitored directly with ^{1}H NMR, with HP Xe and by BET measurements, revealing more complex behavior.

Introduction

The importance of microporous solids such as zeolites[1] and zeosils[2] in processes such as separation, purification, catalysis, stereoselective synthesis, the preservation of unstable or unusual chemical species, etc. is presently indisputable.[3] Microporosity is the fundamental and permanent property particular to this general class of sorbents, with specific functional behavior attributable to the topological and chemical characteristics of the microporous framework. The great success in designing novel zeolitic frameworks for scientific and technological purposes has resulted in their thorough exploration thus also revealing some of the limitations of the covalently bonded, hard zeolite frameworks. “Soft” microporous frameworks, based on the assembly of organic or metal-organic building blocks, have considerable advantages for purposes of design, as there is a near-infinite variability in the building blocks that can be used to assemble zeolite mimics.[4−6] The synthesis of such materials is similar to that of zeolites in that it also involves templating species around which the framework crystallizes or assembles to generate void space. Today, popular design features include large pore volumes, and sufficient robustness so that the pore structure remains intact upon removal of the templating guest species. The net aim of such design is thus again the attainment of permanent pore space with a designed functional topology and chemistry.

However, today another emerging concept for the design of the next generation of materials is where external stimuli cause an intentional response in the functional properties of the material. Such “smart materials”[7] possess structural elements that will allow a rearrangement or transformation in structure, elements that may be built into soft materials rather more easily than into the hard microporous frameworks that are destroyed irreversibly upon conversion to a dense form. The robustness of a framework then becomes a variable design element rather

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than a feature to be maximized, and microporosity becomes a programmable function. Suitable materials include those that can exist in dense and open forms, preferably with relatively easily controlled coordinates for the polymorphic transformations. Recently[8,9] we have described a new metal-organic framework that demonstrated considerable robustness in the absence of the templating guest and, at the same time, a remarkable ability to convert from a dense to an open form in a simple way.

In our endeavors to place this process under full control we faced two principal problems. The first was to define ways of simple, rapid, and reversible switching between open and dense forms. The second was to find suitable methods to follow the processes in situ at the molecular level. For nearly 20 years, ^{129}Xe NMR has been used to probe materials for porosity, with the chemical shift generally diagnostic of the pore system.[10] Often, materials were studied by recording Xe spectra as a function of xenon pressure, with the extrapolated "zero pressure" chemical shift taken as characteristic of the framework. Over the last 10 years, developments in the optical polarization of xenon have enhanced the sensitivity of ^{129}Xe NMR spectroscopy remarkably.[11] Especially the development of a flow system for the continuous production of low concentrations of hyperpolarized Xe that can be integrated into NMR probe technology has great promise for the study of materials and processes.[12] With the use of recently developed NMR methods employing the use of hyperpolarized xenon delivered to an NMR probe, we present an example of a programmable sorbent, where a zeolite-like porous microstructure may be generated reversibly under complete control and with direct monitoring of the structure and microporosity.

Results and Discussion

Molecular-Level Control. From our previous work,[8,9] the [CuL$_2$] complex (L = L$^-$ = CF$_3$COCHCOC(OCH$_3$)(CH$_3$)$_2$) has a molecular structure with the Cu(II) center chelated in the plane by two substituted β-diketonate ligands (Figure 1). There is also secondary, apical coordination of the $-$OCH$_3$ oxygens or $-$CF$_3$ fluorines to the metal centers of neighboring molecules that results in a 3D polymeric assembly, taking on either the dense α or open β form. Only the latter has channels and is capable of sorbing guest species. In the α form, the assembly has both cis and trans isomers in 1:1 mole ratio, whereas in the β form all the units are trans configured (Figure 1). The α-to-β switch thus involves not only a re-assembly of the complex units, but also a chemical, molecular-level change, as isomerization is not possible without breaking Cu$-$O bonds.[13]

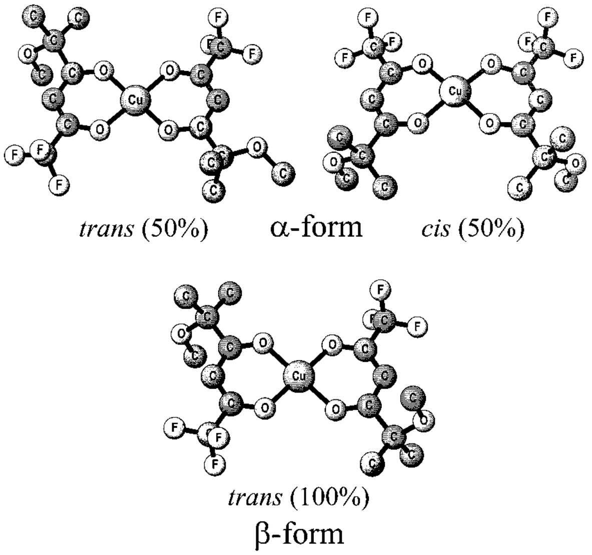

Figure 1. Isomer distribution for the two polymorphs of [CuL$_2$]. The α form has both trans and cis isomer units (top) whereas in the β form they are all trans (bottom).

Our earlier experiments revealed two possible ways of inducing isomerization. The first[8,9] was a change catalyzed by a variety of organic agents, where the α form transforms to β inclusions either in an atmosphere of the agent or upon wetting with the agent. The process may take from hours to seconds[8,9] depending on the material used and the experimental conditions (vapor pressure, temperature, and history of host material). The second way is complementary to the first, as it is very effective for the reverse β-to-α conversion. DSC measurements of the β form (5 deg/min scan rate) revealed an exotherm with a maximum at 75 °C, and the recovered heated sample turned out to be the α form. At temperatures $>$100 °C the conversion occurs practically instantaneously, thus satisfying the requirements for process control.

Sorption Properties of the β Form. The profile of the 1D channel found previously for the β inclusion with benzene[8] is shown in Figure 2. The procedure starts by calculating the diameter of the largest possible inscribed sphere that is in van der Waals contact with the channel walls at the unit cell edge. The profile results when the calculation is carried out as a function of position along the channel axis. Note that the channel is not actually cylindrical and thus it possesses more available space for potential guest absorbates. Several typical guest molecules are shown in the same figure and on the same scale; the channel clearly is seen to allow free passage of the guests along the channel through the structure. There are "necks" separating larger and smaller guest sites that alternate along the channel, and the filling of each site, both large and small, with a guest molecule results in 1:2/3 host:guest stoichiometry.[14]

Figure 3 shows the isotherm obtained for methylene chloride adsorption into the β form. The process is significant over the entire range of guest pressures, reaching a ~0.67 guest per host

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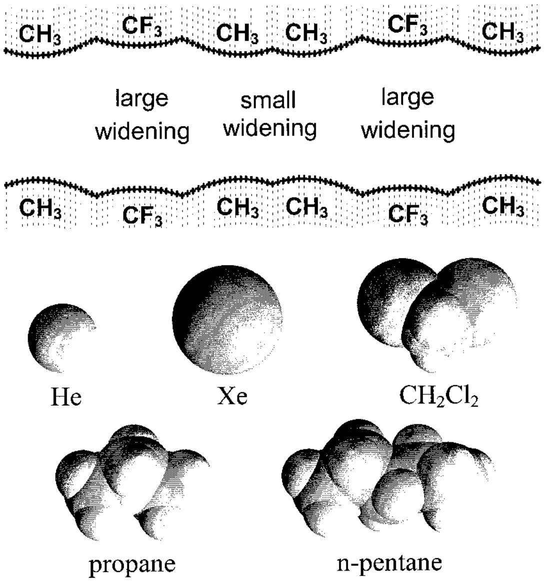

Figure 2. Profile of the 1D channel in β-[CuL$_2$] (see text), with a segment shown consisting of two periods along the crystallographic *c* axis. The location of large and small guest sites and the groups forming the channel walls are shown. Typical sorbate molecules (van der Waals dimensions) are shown on the same scale.

ratio that corresponds to 11.7 wt % of methylene chloride. The sorption is reversible, and is thus consistent with the ability of guest molecules to pass through the channel without serious sterical problems (cf. Figure 2). The shape of the isotherm shows it to be Type I in Brunauer's classification[15] and is characteristic of solids containing micropores.[16] Enhanced sorption in micropores causes a sharp rise of the isotherm before reaching a plateau corresponding to saturation. That sorption is purely physical is illustrated in the same figure (bottom) where the isotherm is outlined as a function $(P_{\text{guest}}/x)(P_{\text{guest}})$. It is thus satisfactorily described by a Langmuir equation $x = x_{\max}[KP_{\text{guest}}/(1 + KP_{\text{guest}})]$, where x is the equilibrium (absorbed guest)−(host sorbent) mole ratio at a guest pressure P_{guest}, $x_{\max}$ is the maximum value of x, and K is a sorption constant transformed to $P_{\text{guest}}/x = (1/x_{\max}K) + (P_{\text{guest}}/x_{\max})$. The experimental data give $x_{\max} = 0.678(3)$ and $K = 0.16(1)$ Torr^{-1}, so that at a given guest vapor pressure x may be directly calculated (valid for methylene chloride guest at 25 °C).

The isotherm for propane is shown in Figure 4. It reveals very similar features. Although the guest:host mole ratio does not reach a value of 2/3 at the guest pressures studied, the ratio derived from the Langmuir equation $x_{\max} = 0.657(6)$, which suggests that the same limits apply on the stoichiometry and sorption behavior as for methylene chloride. There is a quantitative difference as the constant $K = 0.019(1)$ Torr^{-1} is approximately one order of magnitude lower. Again x can be calculated exactly from the appropriate equation and constants.

The results show the β form to be an efficient, zeolite-like sorbent material, capable of sorption over a wide range of guest pressures, able to absorb significant quantities reversibly, and with an excellent degree of both qualitative and quantitative predictability. However, unlike for zeolites and other common sorbents, this sorbent may be "switched off" by being temporarily transformed into the dense (α) form at any time.

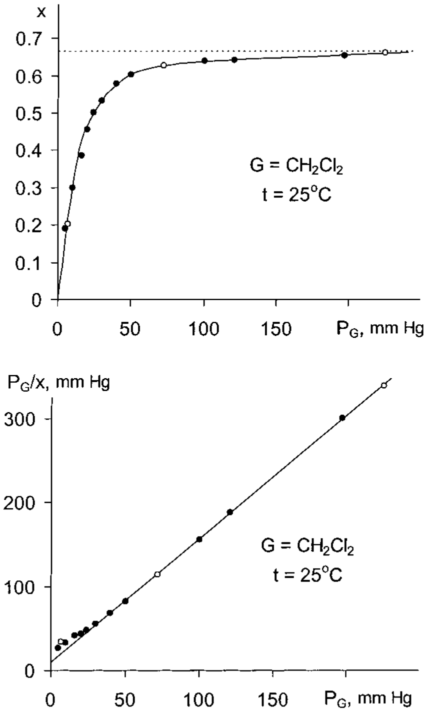

Figure 3. The sorption isotherm (25 °C) of methylene chloride in β-[CuL$_2$] given in conventional (top) and Langmuir (bottom) coordinates. x is the guest to host mole ratio; P_G is the partial pressure of methylene chloride guest (Torr). Dashes in the top figure trace the expected limiting guest-to-host stoichiometry of 2/3 (each site filled with one guest molecule). Open circles indicate points obtained by approaching equilibrium from low guest pressures whereas solid circles indicate those obtained in the reverse direction.

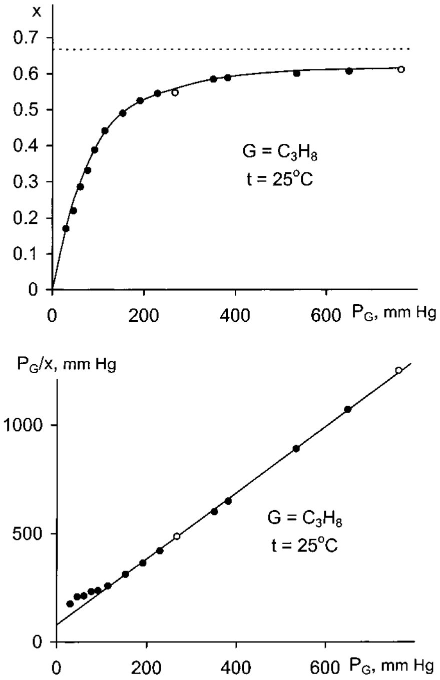

Figure 4. Sorption isotherm (25 °C) of propane in β-[CuL$_2$] given in conventional (top) and Langmuir (bottom) coordinates. For other details see comments to Figure 3.

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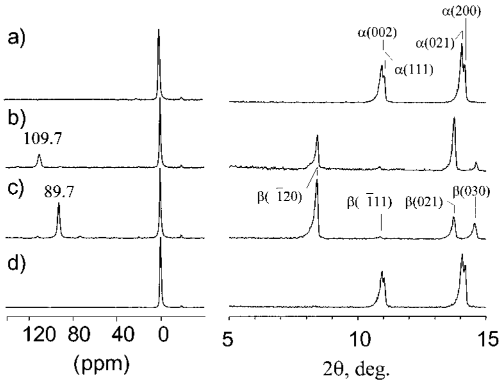

Figure 5. ^{129}Xe MAS NMR spectra (on the left) and powder diffractograms (λ(Co $K\alpha$) = 1.7902 Å) (on the right) of (a) a sample of α-[CuL$_2$] (^{129}Xe NMR spectrum shows only the xenon gas-phase line, and the powder diffractogram shows lines belonging to the α form only), (b) the same sample transformed into the β form filled with methylene chloride guest (there is a weak extra line due to xenon absorbed in micropores and the powder diffractogram has been completely changed); (c) the same sample after removing guest methylene chloride from the pores (the resonance due to xenon absorbed in the micropores increases in intensity and experiences a shift; the powder reflections change in intensities but not in position); and (d) the same sample after applying a heat pulse (70 °C), demonstrating the return to the dense α modification.

This property gives the material an unprecedented potential as a programmable sorbent.

NMR Spectroscopy as a Monitor of Guest Species Inclusion. The ^{129}Xe NMR spectra of the α (Figure 5a) and β (Figure 5c) forms of [CuL$_2$] obtained in the presence of flowing gas (1% Xe) reveal the following features. The first spectrum shows that porosity is absent, as there are no resonances other than the gas line at ~0 ppm. The spectrum of the β form, obtained under both static and spinning conditions, is characteristic of the channel in this material. The signal is remarkably well defined despite the presence of paramagnetic Cu(II) centers incorporated in the material. Consideration of the crystal structure of the β form reveals that the shortest distance between Cu(II) centers and the channel wall is 4.35 Å, and the separation between Cu(II) and in-channel ^{129}Xe nuclei thus exceeds 6 Å. The fact that fine structure is not evident in the static pattern must be attributed to the fact that both anisotropic chemical shift and complex paramagnetic interactions are present simultaneously, perhaps modified by dynamics. Hence, the shift cannot be interpreted easily either from correlations derived for diamagnetic materials. A calculation of the type carried out by Jameson et al.[17] would be required if the magnetic properties of the material could be taken into account.

As well, in some cases we were able to monitor the ^{1}H NMR signal from the included guest directly. This appeared as a sharp resonance with a series of sidebands overlying the very broad signal arising from protons of the host complex. The intensity of the sidebands reflects the degree of motional averaging, with very strong bands observed for pentane, whereas for included methylene chloride and propane they were weaker, indicating a greater degree of dynamic averaging for the smaller molecules. Integration of the proton spectra, followed by subtraction of the broad host signal, gave independent information on the quantity of guest absorbed. Thus both techniques are suitable for probing the material for porosity and following the sorption process without the need for recovering the sample.

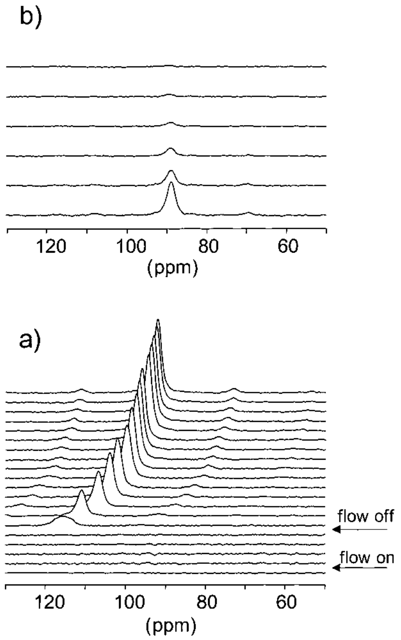

Figure 6. In situ transformation between α and β forms of [CuL$_2$] monitored by ^{129}Xe NMR spectroscopy: (a) α to β transformation in the flow of methylene chloride and (b) β to α transformation at 70 °C. Spectra accumulated over a 5 min. period. Note that for spectrum a the chemical shift changes with time while in spectrum b it is time independent.

In Situ Switching Experiments with Methylene Chloride. The in situ performance of the material as sorbent can be judged by mixing absorbate (methylene chloride in this case) into the gas mixture containing small quantities of HP xenon. Figure 5 shows one cycle of switching between the α and β forms. (Though the whole cycle was performed in situ, in the same figure are given powder diffractograms of the recovered samples from parallel experiments.) The α form (Figure 5a) shows no porosity. Adding methylene chloride (30 cm^3/min total flow with ~300 Torr of methylene chloride over 1 h) transforms the α form to the β form, leaving the latter occupied by methylene chloride. This is attested by the appearance of the weak low-field signal in the Xe spectrum (Figure 5b, left) and the change in the powder diffractogram (Figure 5b, right). Upon stripping methylene chloride out of the channel by the helium gas flow, the low-field Xe signal shifts from 109.7 to 89.7 ppm and becomes far more intense (Figure 5c, left). At the same time, the powder diffractogram changes to that of the empty β matrix (Figure 5c, right).[8] Finally, the application of a heat pulse (70 °C) causes the reverse β to α transformation, thus switching off the sorbent functionality (Figure 5d).

Figure 6 shows how the processes described proceed with time. It should be noted that the experimental conditions were chosen to illustrate the dynamics, but these could be adjusted to advance the point of switching. Shutting off the flow of methylene chloride immediately results in the availability of pore space to xenon that increases with time (Figure 6a). The change in intensity is concomitant with the shift of the HP Xe line, indicating that the effective size of the void space for the xenon molecule also increases dramatically. Evidently this is due to a decrease in total guest content in the void space as the sorption constant for highly volatile xenon and helium must be significantly lower than that for methylene chloride. Previous work has shown that under the flowing gas conditions used, an

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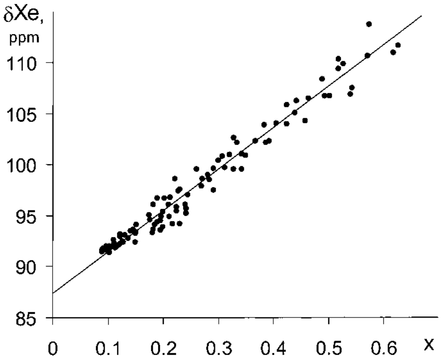

Figure 7. ^{129}Xe chemical shift versus guest per host mole ratio, *x*, with methylene chloride as guest. The points were obtained during dynamic desorption of the guest from the β matrix with a gas flow with zero partial pressure of methylene chloride. Each point was accumulated for 1 min. The equation for the least-squares minimization line is δ_{Xe} (ppm) = 40.7(8)x + 87.4(2) for 100 experimental points.

effectively "zero-pressure" Xe spectrum should result once all "transforming" guests have been removed, as the helium causes a negligible shift. A temperature pulse (Figure 6b) causes the signal intensity to decrease until its complete disappearance signals the completion of the transformation of the β form. The Xe signal does not shift in this instance, indicating that the process is simply a collapse to the α form.

Figure 7 shows that the ^{129}Xe chemical shift versus guest per host ratio x (taken from proton spectra normalized by comparing the intensity of a proton spectrum obtained after a prolonged flow of guest at a partial pressure of 100 Torr with the adsorption isotherm). The data were obtained under dynamic desorption of methylene chloride from the β matrix. As can be seen quite clearly, the data show a linear correlation, thus allowing the direct determination of the degree of filling and the available pore space from the shift. The correlation is described as follows: δ_{Xe} (ppm) = 40.7(8)x + 87.4(2). From this dependence the chemical shifts extrapolate to values characteristic of the empty and completely filled β matrix, 87.4(2) and 114.5(3) ppm, respectively.

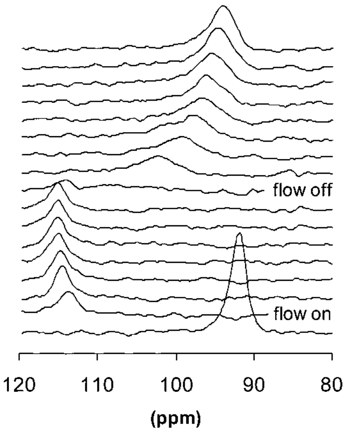

Figure 8. ^{129}Xe MAS NMR spectra recorded during coadsorption of HP xenon and propane on the β-form of [CuL$_2$]. The points of switching of the propane gas flow are indicated. Consecutive spectra were recorded every minute.

The observation of a linear dependence of the chemical shift on the degree of loading can be understood in terms of previous work on the filling of linear channels with xenon.[22] In those cases the chemical shift can be written simply as

$$\delta_{Xe} = Ax + B \tag{1}$$

where x = the fraction of sites filled by xenon. For partial filling of the channels, the chemical shift is a statistically weighted average of the three Xe* chemical shifts, 0Xe*0, 0Xe*Xe, and XeXe*Xe, corresponding to Xe* with 0, 1, or 2 neighbors, respectively, as nearest neighbor effects are the only ones that need to be taken into account, and dynamic processes average the three xenon configurations. We can treat the channel in the [CuL$_2$] system in a similar way; to a first approximation site differences can be neglected and each site in the channel is assumed to host a single guest irrespective of guest type. If Xe and a guest G are sorbed in the channel according to Langmuir behavior, the fraction of sites filled is:

$$x = x_{\max}(K_G P_G + K_{xe} P_{Xe})/(1 + K_G P_G + K_{xe} P_{xe}) \tag{2}$$

where again the K values are the Langmuir constants and the P values refer to the partial pressures. For $K_G \gg K_{xe}$, the terms in K_{xe} can be neglected as P_{xe} is always very small, so that x is just the fraction of sites filled by G. Equation 1 then suggests that δ_{xe} will depend effectively only on the degree of loading of the channel by the guest G. On a molecular level, this can be understood in terms of the chemical shift being a weighted average of the Xe chemical shifts for the situations 0Xe0, 0XeG, and GXeG.

In Situ Experiments with Propane. Propane is unable to act as a template to convert the α form into the β inclusion compound, and thus represents materials that interact only with the microporous β form by adsorption. Remarkably, as long as the β form is already present, either previously loaded or prepared in situ, the qualitative sorption behavior is the same for propane as for methylene chloride. Upon contact of propane vapor (with a partial pressure of ~100 Torr) with the empty β form, the xenon resonance shifts to higher values immediately as the free space available to xenon decreases because of the presence of propane (Figure 8). When the propane flow is switched off, the flowing gas mixture containing HP Xe strips out the remaining propane, as can be seen by the decrease in ^{129}Xe chemical shift, tending to go to a value characteristic of the empty channel. Clearly, it is possible to carry out kinetic studies of sorption and desorption, using the HP Xe chemical shifts to monitor the processes quantitatively, analogous to the situation for methylene chloride.

The relationship between the Xe chemical shift and the fraction of sites filled by propane is linear only at higher pressures and this portion of the plot does not extrapolate to the chemical shift for the empty channel. Clearly, the simple model presented for methylene chloride breaks down. A possible reason is that the Langmuir constant for propane is much smaller than that for methylene chloride, and that xenon may in fact compete with propane for one of the two sites in the channel. If G absorbs preferentially on site A, and Xe on site B, then at low P_G there will be a partitioning of the guests over the two sites, whereas at high P_G, G will again predominate on both sites. At low P_G even small quantities of G will drive Xe

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primarily to the B sites, but if no G is present at all, the Xe chemical shift will be an average over both sites A and B, thus predicting that the high-pressure portion of the curve will extrapolate to a different intercept than the low-pressure portion. Therefore, the chemical shift should depend on the degree of loading in a nonlinear fashion. This additional complexity is not necessarily a weak point of the technique, as it suggests that molecular-scale details of adsorption processes in multisite sorbents become accessible.

Conclusion

We have shown that the processes of molecular isomerization and phase interconversion that trigger the sorption potential of the material are both reversible and controllable in situ by applying appropriate external stimuli such as a specific guest vapor or a temperature pulse. HP Xe NMR is used to monitor these processes and follows the creation and destruction of pore space as well as the degree of filling of the pores by a second component. For strong adsorbers such as methylene chloride, the data are easier to analyze than for weaker adsorbers such as propane where the xenon appears to compete with propane for some sites. This introduces the possibility of competitive binding studies that are likely to shed considerable light on the molecular details of adsorption in complex pore systems. Molecular-level control over functional properties such as porosity can be seen as a first step in designing smart materials for applications such as sorbent actuators or sensors that switch on as sorbents only in the presence of certain sorbates.

Experimental Section

Reagent or analytical grade chemicals were used throughout. The HL (1,1,1-trifluoro-5,5-dimethyl-5-methoxyacetylacetone) and the [CuL_2] complex in pure α and β forms were prepared as described previously.[8,9] Powder diffractograms were recorded on a Rigaku Geigerflex diffractometer (Co $K\alpha$ radiation, $\lambda = 1.7902$ Å). The diffractogram for the inclusion compound with methylene chloride was recorded in an atmosphere of the guest. DSC measurements were performed on a 2920 Modulated Differential Scanning Calorimeter (TA Instruments). Samples of 5 to 10 mg of the empty β form were pressed into aluminum pans and the DSC-curves were recorded at a 5 deg/min heating rate.

For recording the isotherms, a TGA 2050 thermogravimetric analyzer (TA Instruments, RMX-Based Operating System) was adapted. The purge gas system was thoroughly cleaned of volatile impurities with a nitrogen stream before each experiment. All the experiments were performed in the isothermal (25 °C) mode. A sample of ~25 mg of host material was put into the balance pan, the reaction cell was closed, and the system was equilibrated in a nitrogen flow of 50 cm^3/min. Then the flow of reaction gas was added to the nitrogen flow, with the total flow remaining constant.

The original sample used for the methylene chloride isotherm measurements consisted of the powdered α form. The first experimental point was obtained under the maximum guest vapor pressure to transform the entire sample to the β form:

$$\alpha\text{-}[CuL_2]\ (\text{solid}) + x(CH_2Cl_2)\ (\text{gas}) = \beta\text{-}[CuL_2]{*}x(CH_2Cl_2)\ (\text{solid})$$

After the sample weight stabilized, the guest pressure was decreased stepwise to obtain the entire isotherm under desorptive conditions. After that, the pressure was increased again to obtain points for the sorption reaction. Every experimental point took up to several hours for the mass change to come to a plateau value. A nitrogen flow with the required partial pressure of methylene chloride was obtained by bubbling nitrogen gas through neat methylene chloride thermostated at a specific temperature (in most cases at +7 °C) and also by mixing this flow in different proportions with a second flow of nitrogen. With propane, the experimental procedure was very similar, but the empty β form was used as the starting sample, and flows of propane and nitrogen were mixed in different proportions. Because of instrument limitations, there might be enhanced experimental errors in creating gas flows with a low pressure of sorbate in this dynamic method. This is the probable explanation for the deviation of the points from a straight line in Figures 3 and 4 (bottom). The points for pressures less than 30 Torr for methylene chloride and less than 80 Torr for propane were not used in calculations.

NMR spectra were collected on a Bruker MSL 200 NMR spectrometer operating at 200 MHz for ^1H and 55.33 MHz for ^{129}Xe. The probe was a Chemagnetics pencil probe modified[18] so that a stream of gas could be delivered to the spinning sample.[12d−f] The standard gas mixture used had 1% Xe (effective pressure of 7 Torr), 1% N_2, and 98% He. The reaction gas was added to this flow, as required.

The channel profile (Figure 1) was calculated from the crystal structure data on the inclusion compound with benzene[18] using the CLAT[19] program package. The following values for the van der Waals radii (Å) were used:[20] C, 1.71; H, 1.16; Cl, 1.90; F, 1.35; O, 1.29; Cu, 1.40. The same system and the Raster3D[21] program package were used to draw molecules. NMR spectra were analyzed with the WIN NMR program package (Version 950801.1).

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